

## The hydrothermal component in ferromanganese nodules from the southeast Pacific Ocean

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**Abstract**—Statistical analyses of geochemical data from ferromanganese nodule samples representing a broad area of the southeast Pacific Ocean indicate nodule compositions are controlled by four factors: (1) suboxic diagenesis; (2) oxic diagenesis; (3) hydrogenous precipitation; and (4) hydrothermal precipitation. The first three are identical to those identified in studies of nodules from the North Pacific; the fourth factor represents the first quantitative determination of a significant hydrothermal end-member in ferromanganese nodules. Nodules apparently acquire a hydrothermal component through the accretion of colloidal-sized hydrothermal precipitates which are widely dispersed from their origin at vents along the East Pacific Rise (EPR). Nodules recovered from beneath the “shadow” of the present-day hydrothermal plumes emanating from the EPR contain significantly higher amounts of hydrothermal material relative to nodules from other areas.

### INTRODUCTION

ONE OF THE EARLIEST disputes in marine geochemistry concerned the primary source of chemical elements present in ferromanganese nodules. The first such nodules to be studied in detail were those recovered during the voyage of the *HMS Challenger* (1873–1876), described by MURRAY and RENARD (1891). Analyses of these nodules showed they were essentially concretionary oxides of iron and manganese which generally contained high concentrations of certain trace elements and sometimes included minor amounts of silicate and biogenous material. While it appeared that seawater was the immediate source of the elements present in the nodules, MURRAY and RENARD (1891) disagreed concerning the primary source of these elements. Murray suggested the elements in the nodules were derived mainly from volcanic materials and were introduced into seawater through the submarine weathering of basalts, while Renard argued that the nodules acquired their constituent elements primarily from continental runoff and precipitation from normal seawater (MURRAY and RENARD, 1891, as summarized in CRONAN, 1980).

We now recognize that this controversy was based on a false premise, *i.e.*, the idea that a single predominant source is responsible for nodule compositions. Numerous studies subsequently have shown that ferromanganese nodules actually accrue elements from a variety of sources, including volcanic, hydrogenous, continental (ARRHENIUS *et al.*, 1964; CRONAN, 1967) and even cosmic sources (PETTERSSON, 1959), as well as by diagenetic remobilization of metals from the underlying sediments (LYNN and BONATTI, 1965). Hence, the focus of recent inquiry has shifted, such that the problem is no longer to identify a single source for the elements in nodules but rather to distinguish between nodules containing elements from a variety of sources.

The objective of the present study is to identify and quantify the presence of a hydrothermal component in deep-sea ferromanganese nodules. The possibility of hydrothermal con-

tributions to nodule compositions was recognized by BONATTI *et al.* (1972), who included hydrothermal sources as a potential end-member in their qualitative classification scheme of ferromanganese oxide compositions. Yet, until recently, there was little reason to believe that hydrothermal contributions were significant in a quantitative sense. For example, given the oxidizing conditions that commonly prevail in the deep sea, much of the iron and manganese from hydrothermal sources might be expected either to precipitate close to the point of discharge on the sea floor or else to become fractionated from each other over relatively short distances. Thus, both the compositional integrity and areal extent of any hydrothermal “signal” were considered rather limited, other than possibly contributing to the overall manganese content of seawater (LYLE, 1976).

Several recent discoveries serve as a basis for challenging this viewpoint. Sea-floor hydrothermal activity is now recognized as a pervasive marine process, involving substantial fluxes of several elements relative to their fluvial inputs (EDMOND *et al.*, 1982). Measurements of the  $^3\text{He}$  anomaly in seawater (LUPTON and CRAIG, 1981) and the geochemistry of metalliferous sediments in the southeastern Pacific Ocean (DYMOND, 1981; HEATH and DYMOND, 1981) have confirmed that hydrothermal effluents are dispersed over distances of a few thousand km east and west of their sources along the East Pacific Rise (EPR). Moreover, detailed geochemical analyses of both surficial sediments (DYMOND, 1981) and DSDP sediment cores (RUHLIN and OWEN, 1986) have shown that, rather than being fractionated, the iron and manganese content of dispersed hydrothermal precipitates remains highly stable: so stable, in fact, that the Mn/Fe ratio (as well as those of other elements) can serve as a characteristic signal to distinguish the presence of hydrothermally derived material from that of other sources in sediments of widely varying composition (DYMOND, 1981). These observations suggest the hypothesis that the composition of ferromanganese nodules, especially those found beneath the “shadow” of hydrothermal plumes, may contain a significant hydrothermal component. We have examined this hypothesis by conducting various statistical analyses on published data representing nodules recovered from the southeast Pacific Ocean.

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**METHODS**

**1. Experimental design**

The geochemical data for the 76 ferromanganese nodule samples examined in this study (Table 1) were obtained by screening the entire ferromanganese nodule data inventory of the National Geophysical Data Center in Boulder, Colorado, U.S.A. The NGDC inventory consists of information compiled from 544 sources on thousands of ferromanganese nodule samples, including extensive data sets provided by academic institutions and government agencies in France, Germany, Japan, the Soviet Union and the United States. Most of the nodule samples included in this study were recovered

Table 1. Geochemical data for nodule samples examined in this study

No.	Sample <sup>1</sup>		Position		Composition (wt.%)				
	Iden. Code		Lat. (°S)	Long. (°W)	Mn	Fe	Co	Ni	Cu
1	26600180		13.423	134.158	10.2	15.3	0.37	0.79	0.41
2	26600240		10.633	134.867	7.00	10.8	0.03	0.29	0.22
3	26600280		12.850	135.217	31.0	9.10	0.11	9.90	1.20
4	26600281		12.850	135.217	23.9	7.00	0.09	1.46	0.92
5	26600300		13.617	135.517	23.8	11.65	0.12	1.8	0.91
6	26600310		14.983	136.033	12.0	9.80	0.12	0.77	0.53
7	26600311		14.983	136.033	15.2	14.7	0.14	0.90	0.44
8	26600360		12.317	136.950	9.00	10.9	0.10	0.36	0.16
9	26600320		15.383	136.300	23.6	9.82	0.12	1.22	0.50
10	26600322		15.383	136.300	20.3	8.10	0.12	1.17	1.07
11	26600323		15.383	136.300	19.6	18.2	0.14	1.00	0.64
12	26600380		18.967	137.600	16.8	19.6	0.23	0.23	0.22
13	26600381		18.967	137.600	2.88	10.5	0.04	0.09	0.12
14	26700230		17.600	141.917	22.8	23.1	0.70	0.48	0.13
15	26700231		17.600	141.917	16.0	16.2	0.49	0.34	0.09
16	23100040		23.783	140.433	6.00	10.0	0.04	0.40	0.10
17	26100310		13.533	89.083	23.6	10.8	0.10	1.83	0.46
18	26100311		13.533	89.083	21.3	10.5	0.13	0.94	0.41
19	26100341		11.233	89.583	25.1	8.88	0.13	1.11	0.78
20	26100342		11.233	89.583	29.1	11.9	0.11	1.50	0.72
21	26100343		11.233	89.583	31.0	10.5	0.11	1.20	0.67
22	26100344		11.233	89.583	41.7	8.40	0.07	1.50	0.72
23	26100441		11.083	82.517	37.7	4.76	0.05	1.32	0.83
24	26100460		12.417	85.262	29.0	7.36	0.04	1.17	0.92
25	26100480		12.483	87.897	23.9	7.42	0.11	1.50	0.87
26	26200040		10.617	91.317	0.32	1.36	0.01	0.01	0.01
27	26300331		10.633	109.600	38.7	5.50	0.03	0.45	0.83
28	26300510		12.543	101.683	35.1	3.27	0.04	8.95	0.52
29	26300520		12.253	104.228	26.7	7.63	0.05	1.35	0.88
30	26300770		13.683	102.133	28.8	12.7	0.12	1.52	0.60
31	26300771		13.683	102.133	30.9	10.0	0.11	1.74	0.69
32	26100330		18.785	89.433	26.6	8.80	0.24	1.26	0.76
33	26100331		18.785	89.433	47.3	9.59	0.12	1.72	0.71
34	26100332		18.785	89.433	27.8	12.6	0.18	1.70	0.90
35	26100470		17.467	86.700	23.2	9.46	0.08	1.20	0.70
36	26300091		19.192	102.400	21.5	13.3	0.20	1.90	0.74
37	26300093		19.192	102.400	17.2	11.6	0.16	1.52	0.59
38	22600070		21.603	94.933	15.5	10.6	0.18	1.09	0.62
39	22600071		21.603	94.933	18.8	11.5	0.14	0.66	0.24
40	23100110		29.150	143.017	17.7	21.7	0.36	0.46	0.22
41	23100111		29.150	143.017	12.7	15.5	0.26	0.33	0.16
42	19400135		32.600	137.717	16.6	10.0	0.22	0.77	0.30
43	19400161		34.017	138.917	19.6	21.7	0.45	0.50	0.21
44	19400010		39.633	130.217	22.7	11.8	0.30	1.13	0.40
45	19400020		39.633	131.383	20.7	12.0	0.31	0.82	0.41
46	18900021		39.683	131.383	16.60	10.4	0.18	0.82	0.30
47	19400090		35.183	135.533	19.6	14.2	0.73	0.33	0.05
48	19400100		37.083	137.000	18.9	11.2	0.38	0.91	0.43
49	19400101		37.083	137.000	20.2	12.6	0.16	0.82	0.35
50	19400102		37.083	137.000	26.5	11.2	0.28	1.50	0.66
51	19400103		37.083	137.000	24.6	15.4	0.33	0.90	0.53
52	19400110		36.383	137.250	18.7	13.0	0.38	0.69	0.33
53	19400111		36.383	137.250	16.8	13.1	0.43	0.97	0.35
54	19400120		36.550	137.400	14.1	12.4	0.36	0.64	0.29
55	19400121		36.550	137.400	18.1	10.5	0.34	1.10	0.50
56	19400170		35.075	138.662	17.5	15.8	0.43	0.39	0.11
57	19400171		35.075	138.662	19.0	15.8	0.42	0.50	0.18
58	19400172		35.075	138.662	16.0	14.3	0.32	0.42	0.15
59	22500070		25.517	85.233	42.3	2.47	0.17	0.26	0.15
60	22500071		25.517	85.233	37.3	11.2	0.70	0.56	0.16
61	22500076		25.517	85.233	28.8	9.11	0.10	0.32	0.12
62	18900072		33.050	82.050	17.0	13.1	0.11	0.80	0.40
63	18900073		33.050	82.050	16.7	13.8	0.09	0.62	0.37
64	18900140		33.000	85.900	20.6	11.2	0.12	1.21	0.51
65	18900200		32.217	89.450	26.8	19.9	0.16	0.58	0.19
66	18900220		33.075	89.550	22.2	11.2	0.10	1.31	0.57
67	18900230		33.033	84.050	15.5	15.9	0.14	0.50	0.34
68	18900040		37.067	81.833	26.5	9.80	0.11	1.20	0.72
69	18900080		39.950	82.950	23.3	11.4	0.13	1.61	0.47
70	18900081		39.950	82.950	22.3	11.9	0.12	1.01	0.45
71	18900090		37.483	83.117	17.2	12.7	0.12	0.78	0.45
72	18900091		37.483	83.117	18.5	12.3	0.08	0.69	0.34
73	18900092		37.483	83.117	15.4	13.4	0.16	0.80	0.23
74	18900093		37.483	83.117	16.3	15.0	0.16	0.58	0.19
75	19000020		35.733	92.700	14.1	24.7	0.10	0.49	0.21
76	19000071		39.850	96.867	21.3	11.8	0.07	1.13	0.43

1. Sample Nos. were assigned for this study; Sample Nos. 1-16 are from the NW quadrant; Sample Nos. 17-39 from the NE quadrant; Sample Nos. 40-58 from the SW quadrant; and Sample Nos. 59-76 from the SE quadrant (see Fig. 1). Sample Iden. Code numbers are equivalent to NGDC codes.

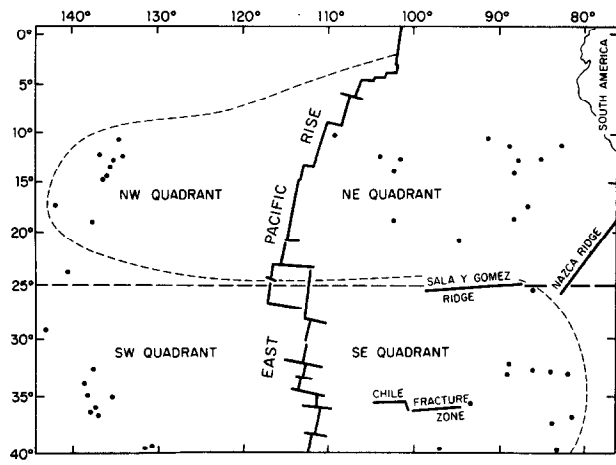


FIG. 1. Map shows locations of nodule samples (black dots) analyzed in this study and dispersal pattern (shorter dashed curves) of hydrothermal effluents (after EDMOND *et al.*, 1982). Quadrants are defined by the EPR (east-west boundary) and an imaginary line (longer dashed line) along 25°S latitude. Note that samples from the NW and SE quadrants lie beneath the "shadow" of hydrothermal plumes, while those in the NE and SW quadrants do not.

during research cruises conducted by the Scripps Institution of Oceanography, Oregon State University, Lamont-Doherty Geological Observatory, Florida State University and Akademiai Nauk (USSR), and were analyzed by investigators from these institutions. In some instances the original geochemical data from these sources were reported to more than the three significant figures shown in Table 1. We have rounded off all original data to three significant figures for the sake of consistency of this investigation.

These 76 nodule samples were collected from a broad, rectangular area of the South Pacific Ocean, ranging from latitude 10°S to 40°S and longitude 80°W to 145°W (Fig. 1). All nodule samples from within this area for which bulk geochemical data for the concentrations of Mn, Fe, Co, Ni and Cu were reported are included in this study. The outer dimensions of this area, as well as the subdivisions defined in this study (see discussion below), are based on the extant mid-depth circulation pattern and its effect on the distribution of hydrothermal precipitates as described by EDMOND *et al.* (1982). These authors note that, due to the markedly asymmetric mid-depth circulation pattern along this portion of the EPR, hydrothermal effluents emanating from the ridge axis are distributed laterally for thousands of km in either an easterly or westerly direction. Flow is predominantly to the east in the southern portion of the study area and to the west in the northern portion (Fig. 1). Relative to the EPR, this pattern results in a pronounced eastern lobe in the distribution of hydrothermal precipitates, centered at about 30 to 35°S (DYMOND, 1981), and a western lobe centered at about 15 to 20°S (HOFFERT *et al.*, 1979). The inflection point between these two lobes lies along 25°S (EDMOND *et al.*, 1982).

The asymmetric distribution of hydrothermal precipitates in this region is fortuitous, inasmuch as it allows us to redefine the study area in terms of a classic block design (*e.g.*, HENLY, 1981) for the purposes of testing various statistical hypotheses. Consequently, we have subdivided the study area into four "quadrants", with the crest of the EPR serving as the east-west boundary and an imaginary line along 25°S (the latitude of current inflection) as the north-south boundary (Fig. 1). Because they enclose the lobes of present-day hydrothermal effluent distribution, the northwest and southeast quadrants are designated here as the "hydrothermal" quadrants, while the northeast and southwest quadrants are referred to as the "background" quadrants. Our objective is to quantify the amount of hydrothermal material in all of the nodules included in this study using an end-member composition factor analysis technique (see discussion below). If hydrothermal emanations from the EPR are incorporated into ferromanganese nodules to an appreciable extent, then the composition of nodules from the "hydrothermal" quadrants should contain

a significantly greater amount of hydrothermal material than those nodules recovered from the "background" quadrants. This hypothesis assumes that the existing mid-depth circulation pattern has been extant over a sufficient time-span to affect nodule compositions. Our statistical tests should provide insight concerning the validity of this assumption.

The four-quadrant experimental design also allows us to control other factors which might otherwise introduce uncertainty into our results. The two factors of greatest concern here are the possible influence of (1) biogenous inputs from the highly productive equatorial region north of the study area and (2) terrigenous inputs from the South American land mass east of the study area. Each of these factors has been evaluated through paired comparisons of compositional data from the nodules in each of the four quadrants.

## 2. Statistical methods

Until recently, geochemists have had limited success in their attempts to determine the composition of end-members in various geologic mixtures using Q-mode factor analysis. The major difficulty has been that transformations of the original data during the analysis often produced negative factor scores for some variables, implying that negative "concentrations" of these variables existed in the end-members that were identified. LEINEN and PISIAS (1984) recently have developed a modified version of standard Q-mode factor analysis and have demonstrated quite conclusively that their technique effectively eliminates this problem. The key mathematical modification involves the use of a nonorthogonal rotation of end-member vectors toward the mean vector to bring each of the end-members into positive vector space. In geochemical terms, the Leinen and Piasias method is capable of generating accurate and objective estimates of the end-member compositions of geologic mixtures. We have used this technique to determine both the number and the chemical composition of the significant geochemical end-members which comprise the bulk composition of the nodule samples. The relative amounts of each of these compositional end-members present in each sample were then determined using a normative analysis technique based on linear programming (*e.g.*, OWEN, 1980; DYMOND, 1981; HEATH and DYMOND, 1981; DYMOND *et al.*, 1984). Finally, we have used the Wilcoxon two-sample test to determine if the relative amounts of a particular compositional end-member (*e.g.*, the hydrothermal component) in the nodules from two different quadrants are essentially the same or significantly different (at the  $p < 0.05$  level). This is a non-parametric method, analogous to the more commonly known Students "t" test: its use is preferred here because it is not based on the assumption that the statistical samples being compared are derived from populations that are normally distributed (ALDER and ROESLER, 1977).

## RESULTS AND DISCUSSION

### Identification of the hydrothermal component

The Q-mode factor analysis of the 76 nodule samples revealed that four factors or end-members account for 99.2%

Table 2. Calculated (via factor analysis) composition of geochemical end-members in ferromanganese nodules from the Southeast Pacific Ocean<sup>1</sup>

	Factor 1	Factor 2	Factor 3	Factor 4
Mn(%)	41.3	23.0	10.9	42.2
Fe	1.23	22.0	35.3	4.58
Co	0.00	1.35	0.00	0.05
Ni	2.80	0.57	0.43	0.00
Ca	1.53	0.00	0.22	0.00
% Variance	49.3	33.1	14.1	2.78
% Cum. Variance	49.3	82.4	96.5	99.3

1. Compositions shown are original varimax factor scores transformed according to the technique of Miesch (1976) and rotated according to the method of Leinen and Piasias (1984). Elemental compositions are normalized to a constant sum of 46.9% (see text discussion)

Table 3. Comparison (and interpretation) of the Mn/Fe ratios of the compositional end-members determined for the nodule samples in this study (Table 2) with those reported for MANOP nodules and for hydrothermal sediments from the Southeast Pacific Ocean

This study Factor	Mn/Fe	MANOP Nodules <sup>1</sup>		Hydrothermal Sediment <sup>2</sup> Mn/Fe
		Mn/Fe	Interpretation	
1	33.5	20-70	Suboxic diagenesis	
2	1.04	~1	Hydrogenous precipitation	
3	0.31	---	----	0.28-0.33
4	9.2	5-10	Oxic diagenesis	

1. From Dymond *et al.* (1984).

2. From Dymond and Eklund (1978), Dymond (1981) and Ruhlin and Owen (1986)

of the total variance in the data set. The scaled varimax factor scores for all five variables (Mn, Fe, Co, Ni and Cu) were converted to compositional end-members by extending the factor analysis using MIESCH's (1976) technique of data closure by summing the elemental concentrations to a constant value (see discussion below) and then applying the vector rotation technique of LEINEN and PISIAS (1984). The results of this procedure, *i.e.*, our calculated values for the composition of each of the four end-members in the factor analysis, are summarized in Table 2.

DYMOND *et al.* (1984) investigated the composition of ferromanganese nodules from Manganese Nodule Project (MANOP) sites H, S and R (see Fig. 1 of their study) in the northeastern equatorial Pacific Ocean. Several aspects of their study are relevant to the present investigation, particularly inasmuch as their results greatly facilitated the interpretation of the factor analysis reported here. For example, they found that the composition of the MANOP samples could be accounted for by variable contributions from three accretionary processes: (1) hydrogenous precipitation, *i.e.*, direct precipitation or accumulation of colloidal metal oxides from seawater; (2) oxic diagenesis which involves various reactions in oxidized sediments that add transition metals to nodules; and (3) suboxic diagenesis, *i.e.*, nodule accretion by the diagenetic remobilization of manganese within the sediments. The concentrations of these three end-members in an "average" whole nodule are 1.50, 57.8 and 40.7%, respectively. By multiplying each of these values by the weight percentage of Mn, Fe, Co, Ni and Cu in each end-member (given in Table 6 of their study), we estimate that the sum of these five elements in an average nodule is 46.9%, and we have used this figure to close our data set to a constant sum. However, we emphasize that any comparisons between the predicted composition of the end-members generated in this study and those reported by DYMOND *et al.* (1984) will be done on the basis of inter-element ratios within the end-members, rather than the absolute value of various elements within the end-members. The inter-element ratios of the data reported in Table 2 would remain the same no matter what value was chosen for a constant sum. Consequently, our estimate of 46.9% is simply a first approximation of the sum of the five elements in an "average" nodule and will in no way affect the validity of any comparisons that are made.

Since Mn and Fe are the two major constituents of ferromanganese nodules, the Mn/Fe ratio served as the primary basis for interpreting the Q-mode factor analysis. The Mn/Fe ratios (Table 3) of three of the four factors determined

here fall within the range of values reported for the three end-members of nodule compositions by DYMOND *et al.* (1984). Thus, we suggest that our factors 1, 2 and 4 are analogous to the suboxic diagenesis, hydrogenous precipitation and oxic diagenesis end-members, respectively, determined for nodules collected from the MANOP sites.

Factor 3 is the most intriguing result of the factor analysis in the present study. This factor accounts for 14.1% of the total variance in the data set and is dominated by Fe and Mn. It is the only factor in which Mn/Fe < 1 and the only one that does not obviously correspond to any of the three end-members of nodule composition determined by DYMOND *et al.* (1984). The existence of this factor indicates the presence of an additional compositional end-member in our samples, which either was not present or did not play a major role in influencing the composition of the nodules from MANOP sites H, S and R.

Several investigations (DYMOND and EKLUND, 1978; DYMOND, 1981; GRAYBEAL and HEATH, 1984; RUHLIN and OWEN, 1986) have demonstrated that the presence of a hydrothermal component in a sedimentary mixture can be readily identified and distinguished from materials from other sources on the basis of highly characteristic ratios (particularly Mn/Fe ~0.3) among various elements which are representative of a pure hydrothermal end-member. The Mn/Fe ratio of factor 3 falls within the range of values typically observed for hydrothermal sediments (Table 3). Other inter-element ratios (*e.g.*, Cu, Fe, Co/Fe, Ni/Fe) calculated for factor 3 also strongly agreed with their hydrothermal analogs. Based on this comparison, we interpret factor 3 to represent a hydrothermal end-member and conclude that the nodules in this study contain a significant amount of material derived from hydrothermal activity along the EPR.

#### Distribution of the hydrothermal component

A quantitative estimate of the relative amount of each compositional end-member present in each nodule sample (Table 4) was determined using a normative analysis model. The model assumes the bulk composition of any nodule sample can be accounted for by some linear combination of contributions from each end-member. Optimum solutions for each nodule sample were determined by linear programming. An assessment of the viability of the model is obtained from an examination of the coefficients of determination for the individual elements (*i.e.*, the proportion of the total variance in each parameter, which is explained by the normative analysis model). The coefficients of determination were as follows: Mn = 100%; Fe = 99.8%; Ni = 95.4%; Co = 84.4%; Cu = 75.2%. These values indicate Mn, Fe and Ni maintain a very high degree of compositional integrity and consistent geochemical behavior within each end-member, while there is probably some degree of breakdown in the constant composition assumption for Co and Cu.

The model predicts that all but two (nos. 59 and 60) of the 76 samples contain some amount of hydrothermal material (Table 4). We note that these two exceptional samples were collected at a water depth of 920 m, which is more than 1200 m shallower than the recovery depth of any of the other samples and well above the depth (~3.0 km) at which hy-

Table 4. Weight percent of each compositional end-member (Table 2) present in each nodule sample, as determined by the normative analysis model.

Sample	Factor 1 (suboxic diagenesis)	Factor 2 (Hydrogenous)	Factor 3 (Hydrothermal)	Factor 4 (Oxic diagenesis)
1	23.7	0	76.3	0
2	14.1	5.47	73.8	6.67
3	68.8	8.79	19.8	2.62
4	68.5	9.33	19.4	2.72
5	61.2	0	38.8	0
6	44.8	0	55.2	0
7	35.1	9.78	55.1	0
8	16.9	16.7	58.5	7.90
9	51.2	11.4	26.5	10.9
10	50.0	13.6	24.5	3.91
11	31.9	12.2	52.1	3.86
12	0	20.7	54.2	25.1
13	0	0	100	0
14	1.78	51.1	31.0	16.1
15	1.96	51.0	31.1	16.0
16	16.8	8.45	74.7	0
17	59.3	9.49	31.2	0
18	39.8	12.9	30.1	17.1
19	46.1	11.9	21.2	20.8
20	51.8	8.38	27.8	12.0
21	41.2	7.75	22.1	29.0
22	45.2	3.20	12.6	39.0
23	48.2	2.28	5.36	44.1
24	47.8	2.48	18.3	31.4
25	68.9	11.3	19.7	0.10
26	0	0	100	0
27	15.9	0	5.48	78.6
28	39.3	1.34	1.11	58.2
29	57.9	4.14	21.0	17.1
30	51.4	9.15	29.6	9.86
31	61.5	8.47	21.9	8.13
32	49.5	21.7	14.0	14.8
33	45.3	5.61	11.4	37.7
34	59.0	11.4	29.7	0
35	52.1	7.61	28.2	12.1
36	54.0	0	46.0	0
37	51.2	0	48.8	0
38	50.7	0	49.3	0
39	26.6	14.7	35.5	23.2
40	5.06	30.5	50.4	14.1
41	5.10	30.8	50.0	14.1
42	36.0	27.0	28.4	8.67
43	5.63	36.4	43.2	14.8
44	42.4	28.4	23.0	6.20
45	30.0	31.0	24.3	14.7
46	38.8	21.8	32.6	6.73
47	0.10	72.3	6.21	21.4
48	36.4	41.5	19.3	2.86
49	31.4	15.7	35.9	17.1
50	54.3	24.2	19.8	1.73
51	26.1	26.9	29.1	17.8
52	22.9	39.6	25.2	12.4
53	30.0	41.6	28.4	0
54	24.7	44.8	30.6	0
55	46.3	24.8	29.0	0
56	5.40	43.0	31.7	19.9
57	10.4	40.0	30.7	18.9
58	9.77	35.0	36.3	19.0
59	9.77	0	0	90.2
60	11.3	36.4	0	52.3
61	9.69	6.64	18.5	65.2
62	33.1	11.8	45.6	9.41
63	23.4	9.27	49.2	18.1
64	52.1	12.3	34.4	1.18
65	11.4	10.4	44.1	34.1
66	54.5	9.73	33.7	2.10
67	14.7	14.5	53.7	17.2
68	63.3	9.77	24.9	2.34
69	47.9	12.0	31.0	9.11
70	39.6	11.1	33.8	15.5
71	32.5	13.0	43.4	11.2
72	27.9	7.91	42.6	21.6
73	33.4	18.4	46.3	1.82
74	19.1	16.7	48.7	15.5
75	7.2	8.49	76.2	8.07
76	46.9	6.61	38.0	8.40

drothermal effluents are emitted from the EPR in the study area (EDMOND *et al.*, 1982). In all other cases our results indicate the areal distribution of the hydrothermal end-member is not limited to those samples recovered from locations within the confines of the present-day distribution pattern of hydrothermal effluents (Fig. 1). On the other hand, inspection of the values associated with the hydrothermal end-member (factor 3) in Table 4 does suggest that samples from the postulated "hydrothermal" quadrants (NW and SE) contain significantly greater amounts of hydrothermal material than their counterparts in the "background" (NE and SW) quadrants. This hypothesis was tested by a statistical comparison (Wilcoxon test), for all possible pairings of the four quadrants, of the mean value of the amount of hydro-

thermal component present in the nodules from each quadrant. The results of these tests (in which the 0.05 significance level was used as the criterion for "significant difference") were as follows:

- 1) Nodule samples from both of the postulated "hydrothermal" quadrants contain significantly greater amounts of the hydrothermal end-member than either of the "background" quadrants.
- 2) No significant difference exists between the amount of hydrothermal material in nodules from the two "hydrothermal" quadrants.
- 3) No significant difference exists between the amount of hydrothermal material in nodules from the two "background" quadrants.

The four-quadrant experimental design allows us to evaluate another important aspect of the data. Since the normative analysis model assumes the bulk composition of a nodule sample is essentially the sum of the contributions from the four compositional end-members, any process which tends to increase or decrease the contribution of one end-member will have the opposite effect on all the other end-members. For example, it is conceivable that the relatively high amounts of hydrothermal material in the nodules from the NW and SE quadrants may not be directly due to an enhanced distribution of hydrothermal material in these quadrants, but instead could simply be a reflection of some process which tends to diminish the hydrothermal contribution in the NE and SW quadrants in favor of some other end-member. This type of indirect influence most likely would occur because of processes which favor the suboxic diagenesis end-member (Factor 1) or the hydrogenous precipitation end-member (Factor 2), since each accounts for a greater percentage of the total variance in the data set than the hydrothermal end-member (Factor 3).

Two processes which might be significant in this regard are the influx of biogenous material from the highly productive equatorial zone north of the study area and the influx of terrigenous material from the South American landmass east of the study area. Any significant difference in biogenous inputs would probably be manifested as relatively higher amounts of dissolved trace elements in the overlying waters and greater amounts of organic matter reaching the sediments in the northern half of the study area. This, in turn, could increase the influence of the hydrogenous precipitation and suboxic diagenesis end-members in the nodule samples at the expense of the hydrothermal end-member. An analogous argument can be made for the influx of terrigenous material from the South American landmass, which would have a relatively greater effect on nodules in the two eastern quadrants.

Based on statistical comparison of all possible pairings of the four quadrants, neither of these two possible influences appears to have a discernable effect on the amount of the hydrothermal end-member present in the nodules. For example, any dilution effect due to biogenous and/or terrigenous inputs should be greatest in the NE quadrant, and least in the SW quadrant. Yet the statistical comparison indicates there is no significant difference in the amount of hydrothermal material in the nodules from these two quadrants.

From this, we infer that the higher amounts of the hydrothermal end-member determined for the nodule samples in the NW and SE quadrants are due primarily to the distribution of hydrothermal effluents by the mid-depth current regime and are not simply statistical artifacts resulting from variations in the other end-members.

#### *Accretion and variability of the hydrothermal component*

The relative importance of different sources of elements to nodules depends upon the proximity of the nodules to the sources, the transport and accretion mechanisms involved, and fluctuations in the intensity of the sources (CRONAN, 1980). The observed compositional differences between the four groups of nodules discussed here, as well as between these nodules and the MANOP nodules, are likely the result of variations in one or more of these parameters. For example, both the widespread dispersal and the remarkably constant composition of hydrothermal precipitates in the southeast Pacific suggest that nodules acquire hydrothermal materials through the accretion of colloidal-sized hydrothermal particles (DYMOND, 1984). Nodules which are situated both proximal to and directly beneath the dispersal pathway of plumes emanating from vents should be enriched in hydrothermal materials relative to nodules which are not.

The widespread dispersal of hydrothermal materials in the study area may also have an indirect influence on the relative mix of the oxic and suboxic diagenesis end-members in the nodule samples. The high Mn/Fe ratios characteristic of these diagenetic end-members require a significant degree of Fe and Mn fractionation relative to the amounts present in the hydrothermal end-member (Table 3). Several authors (LYLE *et al.*, 1977; CALVERT *et al.*, 1978; HEIN *et al.*, 1979) have suggested this fractionation occurs as a result of the authigenic formation of Fe-rich smectite (*e.g.*, nontronite), with the smectite serving as the Fe sink and nodules as the Mn sink. Colloidal Fe-Mn oxyhydroxides that form at spreading centers in hydrothermal fluids will undergo early diagenesis to form Fe-rich smectites whenever silica is available for chemisorption (HEATH and DYMOND, 1977; HEIN *et al.*, 1979). The sources of silica in this case would include that released from the dissolution of opaline biogenic silica, which comprises 1 to 5% of the sediments in the study area (LISITZIN, 1972) on a carbonate-free, dry-weight basis, silica present in the hydrothermal effluents, and dissolved silica in water masses transported into the study area from the biologically productive regions lying to the south.

Although the factor analysis provides a quantitative ranking of the influence of each compositional end-member on the total variance in the data set, the physical significance of this ranking is meaningful only on a time-averaged basis. During any given time period, the relative influence of different sources may have been uniform or else may have varied due to non-steady-state processes. For example, in the case of the hydrothermal component, non-steady-state deposition could have resulted from a change in the current patterns which disperse hydrothermal effluents or possibly from pulsations in the intensity of hydrothermal activity in this region. At least four episodes of anomalously high (as much as 20 times Holocene levels) deposition of hydrothermal materials have been documented in the sediments from the EPR at 19°S

between 25 and 29 My (LYLE *et al.*, 1977). Data required to evaluate the temporal aspect of hydrothermal deposition, such as detailed compositional profiles through individual nodules, are not presently available. Consequently, whereas our analyses have highlighted spacial differences in the proportions of hydrothermal materials in the nodule samples, the question of whether or not the nodules record variations in the rate of hydrothermal deposition remains open.

## SUMMARY AND CONCLUSIONS

Numerous investigations since the pioneering work of MURRAY and RENARD (1891) have shown that ferromanganese nodules accumulate elements from various sources, and that the bulk composition of the nodules can be accounted for by variable contributions from different accretionary processes. We have identified and quantified the presence of four distinct factors which control the composition of ferromanganese nodules from a broad area of the southeastern Pacific Ocean. These include (1) suboxic diagenesis, (2) hydrogenous precipitation, (3) hydrothermal precipitates and (4) oxic diagenesis. Three of these four factors are identical to those identified by DYMOND *et al.* (1984) in their study of nodules from MANOP sites in the North Pacific. This suggests that, except for the hydrothermal component, the same general processes are responsible for nodule compositions in both locations. The discovery of a significant hydrothermal end-member in the nodule samples examined in this study is also consistent with the evidence summarized by EDMOND *et al.* (1982) in support of both active hydrothermal venting and widespread dispersal of hydrothermal effluents away from the axis of the EPR in the southeast Pacific.

Three independent investigations of different sedimentary materials from the southeast Pacific, including Nazca Plate surficial sediments (DYMOND, 1981), sediments from DSDP site 598 (RUHLIN and OWEN, 1986) and the nodules in the present study, have each determined that the Mn/Fe ratio of the hydrothermal component is remarkably constant at a value of  $\sim 0.3$ . Apparently, the major element (Fe and Mn) composition of the hydrothermal precipitates becomes fixed as they form and remains essentially constant during their dispersal as colloidal-sized particles and subsequent accretion by the nodules. The results of our analyses suggest that the nodule samples from the two quadrants (NW and SE) which underlie the present-day distribution pattern of hydrothermal effluents also contain significantly higher proportions of hydrothermal materials and, further, that the enrichment of the hydrothermal component in these samples cannot simply be attributed to variable contributions (*e.g.*, dilution effects) involving the other compositional end-members.

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