The geochemistry of hydrothermal and pelagic sediments from the Galapagos Hydrothermal Mounds Field, D.S.D.P. Leg 70

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ABSTRACT. Over 200 sediment samples taken from ten holes drilled in the Galapagos Hydrothermal Mounds Field during D.S.D.P. Leg 70 have been analysed for twenty-one elements. The three main sediment lithologies recognized are siliceous carbonate ooze, Mn-oxide crust, and an Fe-rich silicate (nontronite), the latter two being of hydrothermal origin. The major element composition of the hydrothermal deposits is similar in each mound hole, suggesting that formation conditions and hydrothermal solution composition have been constant both geographically and with time. The large variations which occur in the concentration of some trace elements in the Mn-oxide crusts and in transition metal ratios in the nontronite compared with the pelagic ooze suggests a hydrothermal supply to the mounds of Li, Mo, Pb, and Ba in addition to Mn, Fe, and silica.

The data are compatible with suggestions that the nontronite formed at depth in the pelagic sediment blanket by replacement of biogenic ooze, whilst the Mn crusts formed at or near the sediment-water interface. Pelagic sediments in the mounds which have not been replaced are similar in composition to pelagic sediments from non-mounds holes.

INTERACTION between oceanic crust and sea-water at elevated temperatures at and near active spreading centres is now regarded as a process which may exert a major influence on the overall composition of the oceanic crust and its overlying sediments and sea-water (Bonatti, 1975 and references therein; Bischoff and Dickson, 1975; Humphris and Thompson, 1978a, b; Edmond et al., 1979). The Galapagos Hydrothermal Mounds Field is thought to be a product of such interaction (Hekinian et al., 1978; Williams et al., 1979). Whilst a hydrothermal origin for the mounds is generally accepted, and upward migration of hydrothermal fluids through the mounds has been shown to occur (Maris and Bender, 1982), several different theories have been put forward for their actual information (e.g. Corliss et al., 1978; Natland et al., 1979;

Williams et al., 1979). One of the aims of Leg 70 of the Deep Sea Drilling Project was to return to the area of the mounds and, using a hydraulic piston corer, to obtain for the first time complete and comparatively undisturbed sedimentary sections through the mounds in the hope of increasing our understanding of these deposits, previously subjected to preliminary investigation during and after Leg 54 of the Deep Sea Drilling Project (Hekinian et al., 1978; Varnavas and Cronan, 1981). The present paper presents the results of analysis of some 200 samples from 10 holes in and near hydrothermal mounds.

A description of the Galapagos Hydrothermal Mounds Field (fig. 1) and its tectonic setting is given in Varnavas and Cronan (1981) and is therefore not discussed further here. However, as a result of the findings of Leg 70, many aspects of the lithology and stratigraphy of the mounds have been revised (Honnorez et al., 1981) and a brief summary of these new data is presented here.
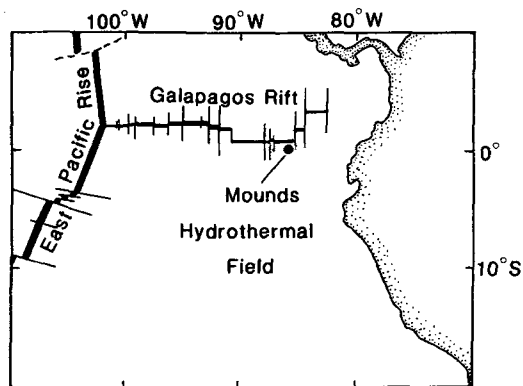

FIG. 1. Map showing location of Galapagos Hydrothermal Mounds Field.

TABLE I. *Table of holes drilled during Leg 70*

Hole	Hole type	Total sediment thickness (m)	Nontronite thickness (m)	Height above basement of lowest nontronite
506	Mound	29	10	11
506B	Near mound	22	0	—
506C	Mound	31	10	10
506D	Near mound	31	0.9	—
507D	Mound	36	15	9
507F	Near mound	31	2	—
507H	Off mound high heat flow	33	0	—
508	Off mound low heat flow	34	0	—
509	Near mound	32	0	—
509B	Mound	33	10	13

LITHOLOGY AND STRATIGRAPHY

A total of ten holes at four sites was drilled in the mounds area; these are listed in Table I. Two major lithologies occur in the mounds region: (1) Pelagic sediments and (2) Hydrothermal sediments.

Pelagic sediments

The typical pelagic sediment in the area is a siliceous foraminifer nannofossil ooze, typically containing 70% or more $CaCO_3$. The biogenic silica content of the sediment decreases from an average of 15% at the surface to almost zero at depth due to the dissolution of siliceous microfossils by warm upwelling hydrothermal solutions (Honnorez et al., 1981). The upper 20–30 cm of pelagic ooze in all the holes drilled is dark brown in colour and constitutes the upper oxidized zone typical of the sediments in this region (Bonatti et al., 1971).

Hydrothermal sediments

Two types of hydrothermal material occur in the mounds and two sub-types of each are recognized.

Mn-oxide material

Mn-oxide crust. Hard fragments of Mn-oxide crust occur in all the mounds holes (506, 506C, 507D, 509B) but are abundant only in hole 509B.

Mn-oxide-rich mud. This sediment type consists essentially of normal pelagic sediment containing abundant finely disseminated Mn-oxide. It occurs only in hole 509B, in the pelagic ooze which caps the Mn-oxide crusts and is not discussed further in this paper.

Nontronite

The predominant hydrothermal material in the mounds is a green Fe-rich mineral of the smectite group, identified as predominantly a nontronite (Corliss et al., 1978; Hekinian et al., 1978) but containing minor amounts of a glauconite-celadonite type mineral (Hoffert et al., 1980). The two sub-types are:

Dark green coarsely granular nontronite.

Paler-green, non-granular, transitional sediment. This lithology typically occurs between normal pelagic sediments and granular nontronite horizons and is regarded as being transitional between the two sediment types.

The nontronite is confined laterally to the mounds themselves. Within the mounds the lowest 7–13 m of sediment is normal pelagic ooze and this is overlain by nontronite, containing wedges of pelagic ooze and capped by Mn-oxide crust, which in turn is overlain by up to 1 m of normal pelagic ooze.

ANALYTICAL RESULTS

After drying and crushing, the samples were completely digested in a mixture of HF, HNO_3 and $HClO_4$. Final solutions, in 1M HCl, were analysed on an ARL 34000 inductively coupled argon plasma spectrometer giving simultaneous determination of K, Mg, Ca, Al, Mn, Fe, Li, Be, Cd, Sr, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ba, and P. Silica was determined by atomic absorption spectrophotometry after a separate digestion in sealed containers using HF and HCl. Accuracy was checked using international standard reference materials and precision, based on replicate analyses, was generally better than 10%.

Mineralogical determinations were carried out on a Phillips X-ray diffractometer using Fe-K_α radiation.

Sediments of the same lithology display similar chemical composition in all holes and no systematic variations in composition with depth occur in any of the ten holes sampled. The chemistry of the sediments is therefore dealt with below on a lithological rather than a hole-by-hole basis.

Pelagic sediments

Surface oxidized layer

The upper oxidized zone of pelagic ooze, described above, was also encountered in the mounds area by Leg 54 of the D.S.D.P. (Dymond *et al.*, 1980) but was not analysed by Varnavas and Cronan (1981). The sediments show a marked enrichment in Mn compared to underlying pelagic ooze (Table II, fig. 2). Ni, Zn, and P show evidence of slight enrichment (Table II). The Mn enrichment is due to its diagenetic remobilization at shallow depth and reprecipitation near the sediment-water interface (Lynn and Bonatti, 1965). However, selective chemical leaching of these sediments (Varnavas *et al.*, 1983) indicates that the other enriched

elements are only partly associated with the Mn-oxide phase in them.

Basal sediment

Basal sediment in many areas on the crest and flanks of the East Pacific Rise has been found to be enriched in Fe, Mn, Cu, Ni, Zn, Pb, and other metals (Boström and Peterson, 1969; Von der Borch and Rex, 1970; Dymond *et al.*, 1973; Sayles and Bischoff, 1973; Cronan, 1976; Heath and Dymond, 1977). Sediment immediately overlying basement was therefore analysed from nine holes drilled in the mounds area. Their average composition is given in Table II. Some variations in minor element content occur but the major element composition of basal sediments from the different hole types (i.e. mounds, near-mounds, off-mounds) shows little variation (fig. 2). Basal sediment from two holes (506 and 507F) appears to be Fe enriched. However, close inspection of the samples shows this simply to be due to contamination with granular nontronite which occurred during coring, and these samples were therefore not included in the averages listed in Table II. As can be seen from fig. 2, the other samples show no affinities with typical basal metalliferous sediments and their Mn, Fe, and Al
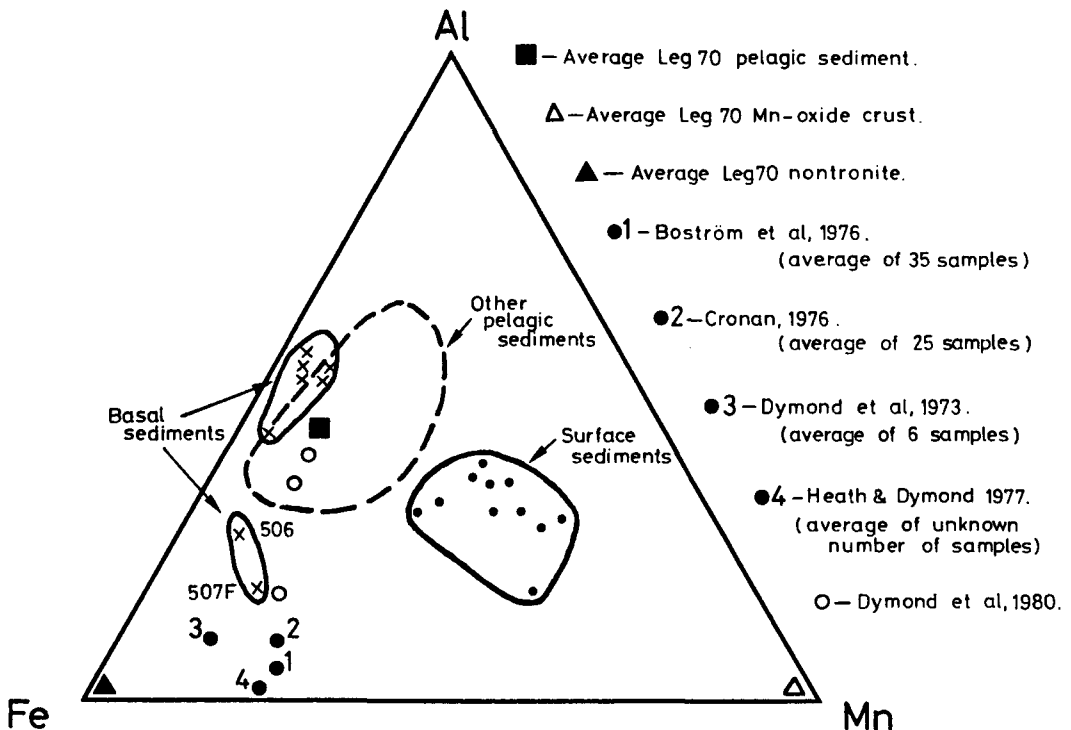

FIG. 2. Fe–Mn–Al ternary diagram of Leg 70 sediment samples and other metalliferous sediments.

TABLE II. *Bulk chemical composition of the different sediment types recognized on Leg 70. For each element the upper row gives the mean and standard deviation whilst the lower row gives the range*

Element		Surface pelagic sediment	Basal pelagic sediment	Other pelagic sediment (carbonate-free value in brackets)		Non-tronites	Transitional sediment (carbonate-free value in brackets)		Mn-oxide crusts
K	%	0.25±0.07	0.22±0.10	0.26±0.09	(0.79)	1.5±0.6	1.1±0.46	(1.2)	0.71±0.35
		0.14–0.34	0.11–0.37	0.1–0.55		0.16–3.42	0.14–2.5		0.21–1.04
Mg		0.65±0.09	0.77±0.30	0.70±0.18	(2.1)	2.2±0.3	2.1±0.5	(2.4)	1.6±0.6
		0.52–0.81	0.43–1.38	0.33–1.1		1.37–3.14	0.77–3.03		0.65–2.12
Ca		23.8±3.0	30.2±3.3	26.8±3.6	—	0.4±0.6	5.4±7.0	—	0.98±0.31
		16.9–29.0	27.0–36.5	15.5–32.8		0.08–3.7	0.14–24.5		0.69–1.50
Al		1.2±0.11	1.2±0.36	1.2±0.36	(3.7)	0.28±0.26	2.2±1.2	(2.5)	0.24±0.09
		1.03–1.39	0.69–1.87	0.49–2.16		0.01–1.12	0.07–5.4		0.14–0.37
SiO$_2$		15.0±1.4	10.0±3.0	14.3±7.4	(43.0)	44.4±4.2	34.3±9.2	(41.1)	3.1±1.6
		12.4–17.2	6.6–15.4	6.9–32.9		29.2–50.3	12.9–49.3		1.5–4.7
Mn		2.1±1.4	0.19±0.16	0.22±0.16	(0.67)	0.11±0.16	0.19±0.28	(0.22)	47.0±5.4
		1.08–5.6	0.08–0.59	0.06–1.16		0.01–1.09	0.03–1.65		44.4–51.8
Fe		1.3±0.4	1.5±0.8	1.3±0.4	(3.8)	20.2±3.2	9.96±4.3	(11.4)	0.66±0.55
		0.93–2.12	0.62–2.68	0.62–2.72		15.5–25.1	1.99–17.5		0.22–1.55
P	ppm	680±160	430±100	440±125	(1330)	250±280	460±180	(530)	1210±250
		505–1020	320–670	224–915		50–1730	95–1190		820–1570
Li		5.1±1.4	7.2±3.8	8.3±2.5	(25)	8.4±7.6	21±9	(24)	100±170
		1.0–6.5	1.2–13.2	< 1.0–15.1		3.1–35	6.1–46		2.5–400
Be		0.3±0.08	0.3±0.14	0.3±0.13	(0.9)	0.27±0.19	0.5±0.35	(0.55)	< 0.2
		< 0.2–0.4	< 0.2–0.5	< 0.2–1.0		< 0.2–1.5	< 0.2–1.6		—
Sr		1050±60	1160±190	1110±160	(3350)	61±46	410±280	(460)	660±260
		950–1150	850–1400	680–1420		19–288	29–1080		290–995
Ti		520±25	570±160	570±200	(1730)	117±115	1000±500	(1130)	28±27
		480–560	400–1890	250–1380		< 2–540	169–2020		< 1–69
V		50±6	58±28	67±25	(200)	17±15	95±67	(109)	107±51
		46–65	29–116	19–136		2–79	9–233		72–185
Cr		30±15	26±14	30±13	(91)	31±11	47±15	(53)	24±15
		8–53	8–55	< 2–61		3–82	15–80		11–48
Co		12±3	8±3	9±4	(27)	3±1.8	10±6	(11)	13±4
		8–16	4–44	3–31		< 1–15	< 2–40		10–22
Ni		161±50	44±13	85±50	(260)	15±11	61±36	(69)	124±64
		67–259	29–212	23–344		< 2–127	9–200		53–255
Cu		102±17	53±19	84±38	(255)	18±15	98±70	(112)	80±62
		85–142	29–102	26–270		< 2–195	6–320		22–180
Zn		177±40	70±22	140±50	(420)	47±30	164±80	(187)	93±37
		144–296	43–124	36–269		14–194	24–365		55–160
Cd		1.8±0.34	1.9±0.4	2.1±0.9	(6.4)	4.2±3.3	3.4±2.0	(3.8)	2.3±1.7
		< 1.0–2.0	< 1.0–2.4	< 1.0–4.4		< 1.0–13.6	< 1.0–8.7		< 1.0–4.5
Pb		18±10	22±7	20±16	(61)	14±10	21±16	(24)	74±75
		< 5–32	< 5–34	< 5–94		< 5–84	< 5–84		< 5–177
Mo		6.5±2	±	5.1±0.3	(15.4)	6.6±2.0	6.8±3.6	(6.9)	540±200
		< 1.0–8		< 1–13		< 1.0–11	2.0–20		200–750
Ba		—	—	—		—	—		2400±1100
									700–3990

content is virtually indistinguishable from overlying pelagic sediment. The metal enrichments seen by Dymond *et al.* (1980) in Leg 54 basal sediments may also have been caused by sample contamination, since their samples also are distinctly different to typical basal metalliferous sediment in composition (see fig. 2).

Pelagic sediment other than surface and basal sediment

The average composition of non-surface, non-basal pelagic sediments from all holes is given in Table II. No systematic trends with depth were observed in trace element content in any of the ten holes investigated in the present study. The only

elements which show systematic trends with depth are Ca and SiO_2. In all holes, SiO_2 decreases with depth due to dissolution of biogenic silica, this effect being more marked in mounds than in off-mounds holes (Honnorez et al., 1981) whilst calcium carbonate shows a concomitant increase (see fig. 3).
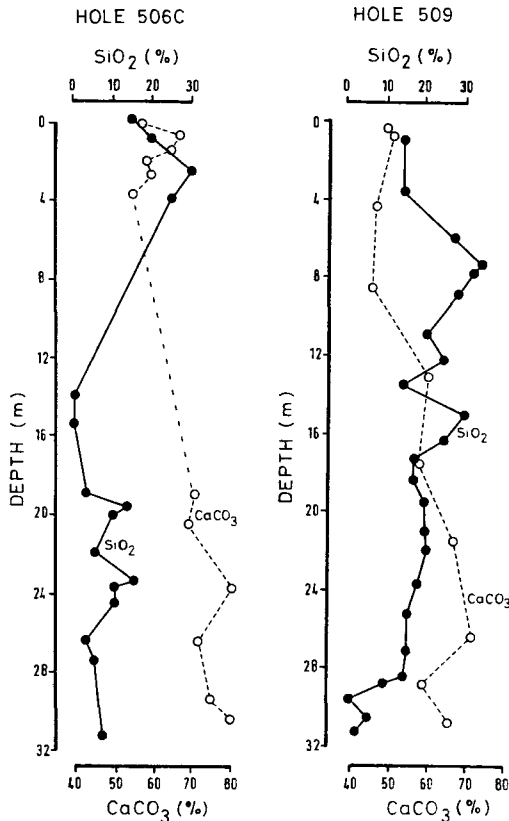

FIG. 3. Variations of $CaCO_3$ and biogenic SiO_2 with depth in a typical mound hole (506C) and non-mound hole (509). $CaCO_3$ data from this study, biogenic SiO_2 data from shipboard smear-slide studies.

Hydrothermal sediments

Manganese-oxide material

The average composition of the eight crust samples analysed is given in Table II. Mineralogically the eight crusts are identical, well-crystalline todorokite being the only mineral identified. Some variations occur in the minor-element content of the crusts. Li is greatly enriched and Ba depleted in hole 507D crusts (average 380 ppm and 760 ppm respectively) compared with crusts from other holes (averages, Li 6 ppm, Ba 2960 ppm). Also the Mo

content of crusts from holes 506 and 507D (720 and 730 ppm respectively) is higher than those from holes 506C and 509D) (average 290 ppm).

The crusts are characterized by very high Mn/Fe ratios and low trace metal contents compared with typical hydrogenous marine Mn deposits, features which are typical of Mn-oxides which receive their metals predominantly by hydrothermal supply (Bonatti et al., 1972; Moore and Vogt, 1976; Toth, 1980) and which indicate a rapid accumulation rate and higher Mn/trace-metal ratios in hydrothermal solutions than in normal sea-water. The comparatively high concentrations of some metals other than Mn in hydrothermal crusts from other localities has led to the suggestion that in some cases they, too, may be supplied by hydrothermal solutions. For example, Zn, after Fe and Mn, has been found to be the transition metal taken into solution in highest concentration by basalt–sea-water interaction at elevated temperatures and pressures (Seyfried and Bischoff, 1977) and this fact prompted Toth (1980) to suggest a hydrothermal source for the elevated Zn contents of several Mn crusts of hydrothermal origin.

Since Co shows no evidence of enrichment in many hydrothermal deposits (Scott et al., 1974; Moore and Vogt, 1976; Hoffert et al., 1978; Toth, 1980) this metal may be used as an indicator of the amount of normal authigenic supply of trace metals to the deposits and a significant increase in metal:Co ratio may therefore indicate a hydrothermal supply of that metal. Table III shows the metal:Co ratios in several of the lithologies analysed in the present study. It is assumed that there is no hydrothermal supply of trace metals to the pelagic sediment. In the Mn-oxide rich samples Ni/Co, Cu/Co, and Zn/Co ratios are similar to those in the pelagic sediment. This infers that there is no significant hydrothermal supply of these metals, relative to Co, to these deposits. Nevertheless, partition geochemical studies (Varnavas et al., in press) indicate that most of the Ni, Cu, Zn, and Co are incorporated in the Mn-oxides, probably having been scavenged from sea-water, but Zn shows some association with Al and may be partly associated with aluminosilicate impurities. The high Pb/Co and Mo/Co ratios in the Mn-oxide samples compared to pelagic sediments suggests that these metals are selectively enriched in the former, and this fact will be discussed later.

Nontronite

Granular nontronite. As can be seen from Table II, the granular nontronite is essentially a fairly pure K, Mg, Fe silicate and the amounts of Mg, Fe, and SiO_2 present vary very little either between mounds or with depth in each mound. Comparison

TABLE III. *Metal: Co ratios in pelagic sediments, Mn-oxide-rich sediment and nontronites*

	Ni/Co	Cu/Co	Zn/Co	Pb/Co	Mo/Co
Surface pelagic sediment	13	9	15	1.5	0.54
Pelagic sediment (mounds)	8	10	16	2.2	0.56
Pelagic sediment (off-mounds)	11	9	15	2.3	0.53
Mn-oxide crust	12	7	11	5.6	42
Mn-oxide-rich mud	17	10	18	4.8	13
Nontronite	5	6	16	5.0	2.2
Pacific Mn-nodules (Cronan, 1975)	1.9	1.1	0.2	0.25	0.13
Continental margin nodules (Cronan, 1972)	13	9	—	0.8	9
Pacific pelagic sediment (Cronan, 1976)	2.1	3.2	1.6	0.7	—

of the composition of the nontronites with the carbonate-free fraction of the pelagic oozes shows that the nontronites are depleted in many elements in increasing order as follows: Li, P, Mn, Zn, Co, Ni, V, Ti, Al, and Ca. Amounts of Be and Pb in quite a few samples were near or below the detection limit and an accurate assessment of their behaviour cannot therefore be made. The very low Al content of the nontronites suggests that not only is the nontronite itself extremely low in Al, but that little extraneous aluminosilicate material is entrained in the nontronite. Partition geochemical studies on nontronite samples (Varnavas and Cronan, 1981; Varnavas et al., 1983) confirm that much of the Al is not present within the nontronite and that the same may be true for Co, Ni, Cu, Zn, and Pb Correlation coefficients for these elements in nontronite samples (Table IV) confirm that at least some of the variability of the elements Co, Ni, and Cu is due to association with adventitious aluminosilicates, and that such material is a major site for V and Ti in the nontronite samples. The site of the Zn and Pb, however, is not clear.

Transitional sediment. Sediment transitional between granular nontronite and normal pelagic sediment was not reported by previous workers on mounds sediments, probably because of the high degree of drilling disturbance encountered by the sampling techniques employed. The major element composition of all transitional sediments, on a carbonate-free basis, is intermediate between average nontronite and average pelagic sediment compositions (Table II), suggesting that transitional sediment is a mixture of these two sediment types. Several elements, such as Al and Ti, do not show the same trend. The reasons for this are quite complex and are therefore discussed elsewhere

(Moorby, 1983) but they do not affect the conclusions drawn here.

Substantial down-core and hole-to-hole variations in composition occur in transitional sediments but they are not systematic and might be ascribed to differences in the relative proportions present of the two principal components, i.e. nontronite and pelagic ooze.

The variations in the proportion of nontronite present in this sediment type allows further examination of the suggestion that many elements in the granular nontronite are present not in the nontronite itself but rather in small amounts of entrained impurities. The transition metals Ti, V, Ni, Cu, and Zn all show a positive correlation with Al and a negative correlation with Fe (Table V). This confirms the suggestion that these elements are concentrated in the non-biogenic component of the pelagic sediment and are present in much lower amounts in the nontronite itself.

DISCUSSION

The completeness of the sediment recovery achieved during Leg 70 enables rough mass-balance calculations to be carried out to determine the source of elements in the hydrothermal deposits. For example, the data presented above show that pelagic sediment beneath the mounds contains similar amounts of Mn and Fe as sediment in non-mounds holes. These elements must therefore be derived exclusively from the basement and be transported by the upward migrating hydrothermal fluids (Honnorez et al., 1981). Assuming that amounts of biogenic SiO_2 in the surface sediment (15–20%, Honnorez et al., 1981) were

Table IV   Correlation coefficients for elements in Leg 70 nontronites.

	K	Mg	Ca	Al	Mn	Fe	Li	Sr	Ti	V	Co	Ni	Cu	Zn	Pb	P
Mg	.53															
Ca		.28														
Al																
Mn																
Fe	-.26	-.25														
Li		.58	.46													
Sr		.58														
Ti				.93												
V				.70					.72							
Co				.39					.39	.43						
Ni				.51			.32	.33	.51	.79	.58					
Cu				.63					.65	.75	.49	.83				
Zn												.31				
Pb																
P						.66							.42			
Mo															.51	

Sample population = 88

Minimum significant correlation at 99% confidence level = 0.25

Table V   Correlation coefficient for elements in Leg 70 transitional sediments.

	K	Mg	Ca	Al	Mn	Fe	Li	Sr	Ti	V	Cr	Co	Ni	Cu	Zn	Pb	P	Mo
Mg																		
Ca	-.55	-.69																
Al			-.38															
Mn		-.37																
Fe	.48	.64	-.52	-.52	-.38													
Li		.42	-.39	.58														
Sr			.56			-.40												
Ti				.95		-.51	.66											
V				.36		-.36	.52		.45									
Cr				.45			.36		.56									
Co							.44		.32	.74								
Ni				.37	.45	-.47	.44		.44	.38		.62						
Cu				.34		-.37	.35		.38	.42	.39	.39	.58					
Zn				.57		-.43	.69		.65	.60	.42	.56	.72	.57				
Pb				.47									.42					
P				.43					.51		.52				.38			
Mo							-.40											

Sample population = 58

Minimum significant correlation at 99% confidence level = 0.32

originally present throughout the sediment column it can be calculated that in the four mounds cored only up to half the SiO_2 in the nontronite could be supplied from the dissolution of biogenic remains in the underlying pelagic sediment. Much of the SiO_2 and all the Mn and Fe in the nontronite and Mn-oxide crusts must therefore be of hydrothermal origin.

The behaviour of several other elements suggests that they too may be supplied in significant amounts by hydrothermal solutions. For example, Barrett and Friedrichsen (1982) have shown, on the basis of Pb-isotope studies, that there is a large basaltic contribution of Pb to the nontronites and probably to the Mn-oxide crusts also. The Pb/Co ratio of both crusts and nontronite (Table III) suggests excess supply of Pb over Co compared to the normal authigenic supply as reflected in Leg 70 pelagic sediments and Pacific deep-sea nodules. Surface pelagic sediment and continental margin nodules also show low Pb/Co values (Table III) indicating that diagenetic processes cannot explain the increase in the Pb/Co ratios. Since the pelagic sediments beneath the hydrothermal deposits in the mounds are not depleted in Pb compared to sediment in off-mounds holes, flushing of Pb out of pelagic sediment by hydrothermal solutions may also be discounted. A hydrothermal contribution of Pb to both Mn-oxide crusts and nontronite must therefore have occurred.

Mn-oxide crust samples, particularly those from holes 506 and 507D are high in Mo. Continental margin nodules also show enrichment in Mo and high Mo/trace-metal ratios compared to deep-sea nodules (Cronan, 1975). This is thought to be due to diagenetic enrichment of Mo relative to other trace metals. However as can be seen from Table III the Mo/Co ratio of Leg 70 Mn-oxide crusts is far higher even than in continental margin nodules and this implies a hydrothermal supply of Mo to the deposits.

Ba is also present in most crusts at levels higher than those typically found in deep ocean or continental margin Mn-nodules (Calvert and Price, 1977). Grill et al. (1981) found equally high Ba contents in several crusts from the Explorer Ridge in the north-east Pacific Ocean. They suggested that this was due to a hydrothermal supply of this element. Certainly, Ba enrichment in sediments of hydrothermal origin is well documented (Boström and Peterson, 1969; Boström et al., 1973; Heath and Dymond, 1977). It seems likely therefore that at least some of the Ba in Leg 70 Mn-oxide crusts is of hydrothermal origin.

Edmond et al. (1982) have shown that exiting hydrothermal solutions at the Galapagos Spreading Centre are greatly enriched in Li compared to normal sea-water and the high Li values in the Mn-oxide crusts may therefore be a result of hydrothermal supply.

Mn in upwelling hydrothermal solutions is only likely to be oxidized and precipitated at, or very close to, the sediment-water interface. Considerable mixing is therefore likely to occur between hydrothermal solutions, the bottom water, and uppermost interstitial pore waters, before and during the precipitation of the Mn-oxide crusts. Variations in the degree of the mixing may lead to selective precipitation and incorporation of elements and thus to variations in compositions between the crust samples analysed.

Harder (1976) has shown that nontronite precipitation occurs in more reducing conditions than those required for Mn precipitation. Thus in contrast to the Mn-oxide crusts, the nontronite in the mounds is likely to have formed at depth, probably by replacement of pre-existing pelagic sediment. In such circumstances little mixing of hydrothermal solutions with bottom waters is likely. The generally constant major element content of the nontronite in different mounds would suggest a uniform composition of the hydrothermal solutions both geographically and with time, and suggests that the conditions under which it formed have remained stable with time.

As discussed earlier, most of the elements determined show strong depletion in nontronite compared with pelagic sediment, a feature also noticed by Varnavas and Cronan (1981). These authors suggest that one reason for the depletion of the hydrothermal deposits in elements such as Ni, Cu, and Zn may be the precipitation of these elements as sulphides at higher temperatures, within the basement. Elements such as Co and V however probably do not precipitate at depth. Their low concentration is more likely to be due either to their not being leached during basalt-sea-water interactions or because crystallographic constraints limit their ability to become incorporated in the hydrothermal deposits.

The elements Mo and Li do not show the strong depletion displayed by other trace elements in the hydrothermal deposits. A hydrothermal supply of Li and Mo to the mounds has already been suggested to explain the elevated levels of these elements in the Mn-oxide crusts. High levels of these elements in the hydrothermal solutions could lead to their incorporation in the nontronite also, Li in an inter-layer site analagous to K, but Mo, because of its high ionic charge probably in an octahedral site.

The behaviour of the trace elements in the sediments suggests that in the granular nontronite they are largely adventitious and that the variations

which occur in minor-element content of non-tronite samples probably reflect different amounts of non-hydrothermal material entrained within the nontronite. This material is likely to be the non-biogenic fraction of the pelagic sediment since both biogenic silica and carbonate are dissolved from the sediments in the mounds. Loss of biogenic silica, which becomes more marked with increasing depth (see fig. 3), occurs because of its dissolution by warm hydrothermal solutions (Honnorez et al., 1981). Dissolution of calcium carbonate occurs because of the drop in pH caused by nontronite precipitation (op. cit.) and this dissolution is therefore confined to horizons close to the site of nontronite formation. These dissolution processes explain why the non-tronite horizons are so pure even though they form within existing sediments.

Seyfried and Mottle (1977) suggest that sea-water reacting with basalt in a water-dominated system produces a solution which is greatly enriched in Mn, Fe, and SiO_2 and depleted in Mg relative to original sea-water, levels of K remaining about the same. Although Al is also leached in this process, Fe is released to a far greater extent such that the Fe/Al ratio in the resulting solution is over 300 compared to an Fe/Al ratio of normal sea-water of approximately 1 (Murray and Brewer, 1977). Such conclusions are in complete accordance with the compositions of the hydrothermal deposits described here and suggest that the hydrothermal solutions feeding the mounds are part of a water-dominated hydrothermal circulation system beneath the area. The low exit temperatures of the solutions (Honnorez et al., 1981) also indicate that the system is water-dominated.

The lack of extensive alteration in the upper part of the basement and the low temperatures prevalent there (Honnorez et al., 1981) suggest that the source of these solutions lies at some considerable depth. We thus favour the idea of a single large feeding convection cell within the basement rather than a series of shallower, smaller ones.

Our chemical data are in complete accordance with the theory of mounds formation, proposed by Honnorez et al. (1981), involving development of nontronite at depth in the sediment column, and commencing about 300 000 years B.P. As these authors suggest, this process may involve reduction of buried Mn oxides which subsequently reprecipitate at the sediment–water interface. The buried nature of the Mn-crusts recovered on Leg 70 implies that the mounds are presently inactive, at least where cored, but the interfingered nature of nontronite and pelagic ooze within the mounds suggests that activity is probably episodic in a single mound even if upwelling of hydrothermal solutions is continuous in the area as a whole.

Normal pelagic sedimentation has therefore occurred in the area before, during and since the hydrothermal activity giving rise to the mounds. Where hydrothermal deposition has occurred within the sediment blanket (i.e. nontronite formation) this has led to modification and dissolution of the pelagic sediments but beneath, above, and laterally removed from the site of hydrothermal deposition the pelagic sediment blanket has remained unaffected by these processes.

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