

A
thesis
entitled

THE GEOCHEMISTRY AND ENVIRONMENT OF
DEPOSITION OF SOME FERROMANGANESE OXIDE
DEPOSITS FROM THE SOUTH EQUATORIAL PACIFIC

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ANDREW CAMERON APLIN

Royal School of Mines,
Imperial College.

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Abstract

A well-controlled suite of ferromanganese encrustations from the Line Islands Archipelago, representing the hydrogenous end-member of the marine ferromanganese oxide continuum, has been analysed chemically and mineralogically. Although enriched in Co (maximum 1.1%, mean 0.54%) and Mn (maximum 29%, mean 20.4%) compared to SMnO_2 -rich nodules from adjacent basins, the crusts are nevertheless mineralogically and chemically similar to those deposits.

An analysis of variance procedure using depth, latitude and substrate type as independent variables indicates that most chemical variability in the crusts is depth-related. Crusts from between one and two kilometres depth exhibit higher Mn/Fe ratios and different transition element and rare earth element compositions compared to crusts dredged from 2-4.5 km depth. Crusts with high Mn/Fe ratios occur at depths in which a dissolved Mn maximum is found in the water column in association with the oxygen minimum. A model to explain the observed compositional variations is outlined.

Additionally, a suite of Fe-Mn nodules and associated sediments from the S.W. equatorial Pacific has been examined to ascertain possible relationships between nodule chemistry and mineralogy and sediment lithology and geochemistry. By assuming that the composition of the LI crusts represents that of ferromanganese oxides accumulating directly from the water column, variations in the composition of nodules and the hydroxylamine hydrochloride-acetic acid soluble sediment fraction (HSF) are ascribed to variations in element supply and early diagenetic reactions.

The LI crusts, HSFs and SMnO_2 -rich nodules exhibit compositions which are broadly similar but strikingly different to todorokite-rich nodules. Differences between the composition of the crusts and the HSFs are related to processes of element supply rather than diagenesis, whilst the SMnO_2 nodules have compositions explicable in terms of a mixture of LI-type Fe-Mn oxides and the sediment HSF.

Oxic and suboxic early diagenetic reactions which may favour todorokite formation are examined and discussed. Most probably, reactions occurring in an organic-rich surface sediment layer involving the reductive remobilisation of Mn oxide and the release of trace metals from labile sediment components are important in forming these nodules.

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SECTION 1

Ferromanganese crusts from the Line Islands Archipelago,
Central Equatorial Pacific.

CHAPTER 1 INTRODUCTION AND REGIONAL GEOLOGY

1.1 Introduction

Given the vast literature concerning ferromanganese nodules, it is perhaps surprising that such little attention has been focussed on the ferromanganese encrustations which occur on rock substrates. This may in part be due to the lack of interest shown by the marine mining industry, for whilst many of the encrustations lie within the potential 200 mile economic zone of island archipelagos, by their nature they occur in rocky regions of rugged bathymetry difficult for efficient mining activity.

Ferromanganese crusts have been recovered from a number of seamounts and seamount chains (Hamilton 1956, Aumento et al. 1968, Cronan and Tooms 1969, Lonsdale et al. 1972, Heezen et al. 1973, Glasby and Andrews 1977, Colley et al. 1979, Craig et al. 1982, Malahoff et al. 1982), from mid-ocean ridges (Aumento 1969, Glasby 1973a, Scott et al. 1974, Moore and Vogt 1976, Toth 1980, Moorby and Cronan, in press) and from volcanic arcs (Cronan et al. 1982). Many of these studies, in particular those of seamount encrustations, have not however been systematic or detailed since their primary objectives have been geological or geophysical. The exception is Craig et al's (1982) study of a suite of crusts dredged from 800 - 2,000 m in the Hawaiian Archipelago.

Marine ferromanganese deposits may derive metals from four sources (Bonatti et al. 1972, Cronan 1980):-

1. Directly from the water column (hydrogenous deposit)
2. From hydrothermal activity
3. From interstitial pore waters, associated to a greater or lesser extent with early diagenetic reactions in the sediment.
4. From low temperature weathering (halmyrolysis) of submarine rock.

For encrustations developing on hard, rocky substrates we may reject (3) as a metal source. Although we cannot reject hydrothermalism as an ultimate source of metals, away from centres of present-day hydrothermal activity mixing within the water column obscures those original sources. As will be shown, there are fundamental differences between the LI crusts and ferromanganese crusts occurring close to the point of discharge of hydrothermal fluids (Scott et al. 1974, Moore and Vogt 1976, Toth 1980). Encrustations therefore provide an excellent opportunity for studying the hydrogenous end-member of the marine ferromanganese oxide continuum and for examining the possible importance of halmyrolysis as a source of metals. In addition, information may be gleaned concerning the trace-metal enrichment mechanisms of Fe and Mn oxides.

The present work concerns a suite of ferromanganese crusts dredged from the Line Islands Archipelago in the central Pacific Ocean. The samples were recovered by the University of Hawaii's research vessel Kana Keoki in 1979 as part of a study of the structure and evolution of the Line Islands. The study was undertaken because no systematic studies had previously been made of a well-controlled suite of hydrogenous encrustations from such a diversity of depths.

1.2 Regional geology

The bathymetry and tectonic setting of the Line Islands Archipelago (LIA) has been described by Winterer (1976a) and is shown in Fig. 1. The archipelago represents a linear chain of atolls, guyots and seamounts stretching south-east a distance of 3,500 km from Horizon Guyot ($19^{\circ}\text{N } 169^{\circ}\text{W}$) to the Tuamotu Archipelago at 15°S . The northern end of the chain terminates against the mid-Pacific mountains, whilst in the south the archipelago abuts onto the Tuamotu Archipelago forming a dogleg in a similar way to the Hawaiian - Emperor chains to the north. To the west and east are deep basins of Cretaceous age - the

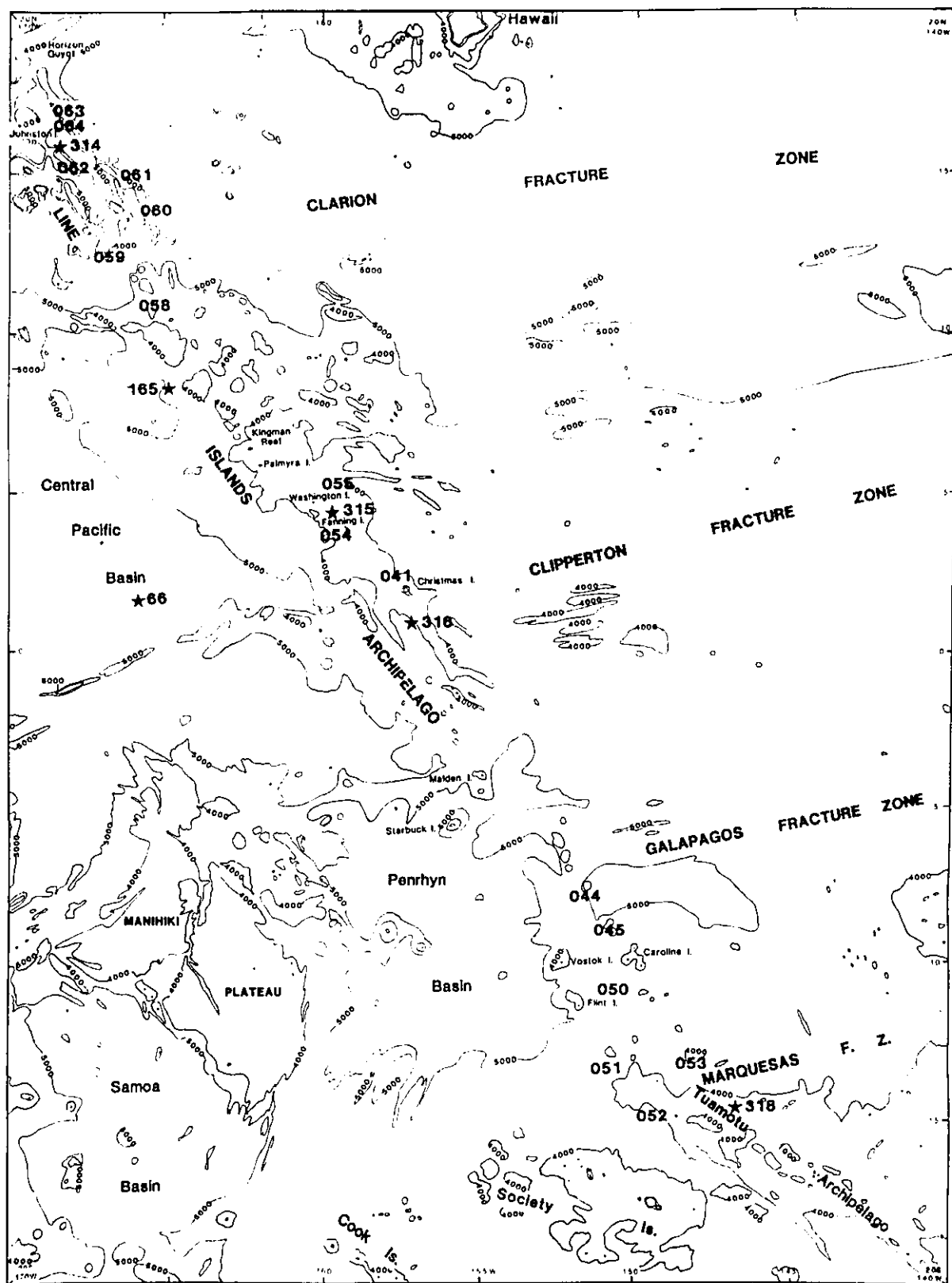


Fig.1. Bathymetry of, and sample locations on the Line Islands Archipelago.

Northeast Pacific Basin, generally deeper than 4,500 m, in the east, and the Central Pacific and Penrhyn Basins, deeper than 5,000 m, in the west.

Throughout its length the chain consists of at least two parallel lines of seamounts and ridges approximately 100 km apart. Another series of ESE trending en echelon ridges and seamounts intersect the main chain from the west at 14° - 16° N, 9° - 10° N and 1° N - 1° S, known collectively as the Line Islands Cross Trend. Winterer (1976b) has suggested that the cross trend represents lines of weakness in the ocean crust produced by a spreading episode around 110 My B.P. This is supported by the work of Orwig and Kroenke (1980) who infer from magnetic and bathymetric data that the Central Basin Rise, which intersects the LIA at 1° N and trends at 260° , was a spreading centre between 100 My and 85 My B.P.

North of the equator much of the region is shallower than 4,000 m; in very few places do passages occur deep enough to allow the flow of Pacific Bottom Water (Normark and Spiess 1976. See Section 8.2). South of the equator positive features are sparser and separated by basin areas deeper than 5,000 m. Steep-sided seamounts and guyots rise to varying depths, often to less than 1,500 m. Several islands occur along the chain (Fig. 1).

1.3 Tectonic history

Developing the proposal of Wilson (1963a) that the Hawaiian volcanic chain was formed in response to the passage of the Pacific plate over a fixed 'hot-spot' in the asthenosphere (upper mantle) and the observation of Christofferson (1968) that the Emperor chain bent north from the Hawaiian chain, Morgan (1972) suggested that the Line Islands and Tuamotu chains were related in a similar way. Several strands of evidence suggest that this is not the case:-

1. The LIA does not show good parallelism to the Emperor chain (Clague and Jarrard 1973).
2. K-Ar dating of late-stage volcanism (Table 1) shows no evidence of a uniform rate of volcanic propagation. Rather, the results are indicative of episodic volcanism throughout the chain; although the majority of dates are between 75 + 85 My, the youngest and oldest dates occur at adjacent sites and ages ranging between 70 + 89 My have been determined for rocks obtained from the same site ($12^{\circ} 31'N$ $167^{\circ} 03'W$). In addition, Saito and Ozima (1976, 1977) have dated basalts at DSDP Site 66 in the Central Pacific Basin at 52 My juxtaposed with late Cretaceous (100-87 My) sediments. Further, considerable differences have been found in the ages of volcanic rocks drilled only 150 km apart at Site 171 ($19^{\circ} 27.6'N$ $169^{\circ} 27.6'W$, 91-100 My, Winterer, Ewing et al. 1973) and Site 313 ($20^{\circ} 10.52'N$ $170^{\circ} 57.15'W$, 72-76 My, DSDP Scientific Staff 1973).
Haggerty et al. (1982) have found basalts associated with Eocene sediments near Caroline Island in the south of the chain.
3. Data from Leg 33 of the DSDP (Jackson and Schlanger 1976), which drilled along the LIA to investigate its development, indicates that carbonate banks developed synchronously throughout the chain at approximately 80 My BP, presumably in response to volcanism building into the photic zone.

Despite the above reservations, the possibility cannot be ruled out that the LIA developed initially in response to passage over a hot-spot, with late-stage volcanism, possibly related to an epeirogenic pulse, destroying the previous record.

An alternative interpretation is given by Orwig and Kroenke (1980), who, having proposed the Central Basin Rise to be a spreading centre active between 100 My and 85 My, suggest that the LIA formed along a large transform fault separating the East Pacific Rise from another active spreading ridge south of the mid-Pacific mountains.

Table 1 K-Ar ages for late-stage volcanism in the Line Islands

Position		Date (My)	Reference
18° 05'N	169° 04'W	128	Saito + Ozima (1976)
13° 28'N	165° 25'W	46 ₊₃	Garcia (pers. comm.)
12° 31'N	167° 03'W	70-89 (3 values)	Garcia (pers. comm.)
12° 04'N	165° 50'W	84.4	Saito + Ozima (1976)
8° 11'N	164° 52'W	79-83	Winterer, Ewing et al. (1973)
4° 10'N	158° 31'W	85	DSDP Scientific Staff (1974)
4° 10'N	158° 31.5'W	85	
00° 06'N	157° 08'W	81-83	DSDP Staff (1974)
(2° 24'N	166° W	52 ₊₅	Saito + Ozima (1976))

1.4 Petrology of the basalts

Generally, the LI volcanic rocks fall within the oceanic island category, with some late stage lavas similar in composition to the post-erosional lavas of the Hawaiian, Samoan and Society chains (Jackson et al. 1976, Natland, 1976). Such rocks are characteristic of mid-plate volcanism and differentiate the LIA from the Manihiki Plateau and surrounding basins, which are formed from basalts of a mid-ocean ridge tholeiitic type.

In detail, the basalts show considerable petrological diversity. Tholeiitic and alkalic basalts have been found in a single dredge haul, and potassic rocks chemically distinct from other known oceanic rocks but similar to certain rocks in the East African Rift have been dredged on seamounts (Natland and Jackson 1976). Such petrological diversity is suggestive of multi-phase volcanism.

To summarize the tectonic history of the LIA:-

1. Hot spot volcanism is an unlikely mechanism for the formation of the archipelago; possibly volcanism took place along a transform fault.
2. The bulk of volcanism, of an oceanic-island type, occurred between 70 + 85 My BP. Sporadic volcanism continued until 40-50 My BP.
3. Volcanism was sufficient to build much of the area above 4,000 m, with many seamounts developing into the photic zone.
4. Rapid volcanoclastic and reefal sedimentation waned by 65 My BP, giving a baseline date for the initial development of Fe-Mn crusts.
5. Subsequent volcanism occurred, at least in parts of the archipelago, in Eocene times.

CHAPTER 2 SAMPLE DESCRIPTION AND SAMPLING TECHNIQUES

Samples of ferromanganese encrustations were obtained at 16 sites between 15°S 149°W at the northern end of the Tuamotu Archipelago and 16° 25'N 168°W at the northern end of the LI Archipelago (Fig. 1). Associated substrates were collected at 14 of the stations. Station details are given in Appendix 1).

The majority of dredging was done on the lower and middle slopes of seamounts where there was a better chance of dredging loose debris (Davis 1980). This is reflected in the diversity of rock types dredged at individual stations. Preliminary rock dredge reports (Appendix 1) typically show volcanic breccia, basalt, limestone, limestone breccia, volcanic sandstones and altered volcanics occurring in the same dredge haul.

2.1 Substrate description

Substrates were examined in hand specimen, crushed, and analysed chemically by atomic absorption spectrophotometry and mineralogically by XRD. Hand specimens are described briefly in Appendix 1, chemical compositions are shown in Table 2 and mineralogical data in Table 3. No petrographic work was attempted.

Although the substrates exhibit highly variable characteristics both within and between stations, they may be placed, on a mineralogical basis, into three categories:-

1. Francolite (carbonate fluorapatite) - samples O55 3/3, O58 2/2, O61 2/5(1), O62 3/3, O63 1/9, O63 5/9, O63 5/9A, O64 5/7.
2. Phillipsite and smectite - samples O50 4/6, O51 2/7, O51 3/7, O51 5/7, O51 6/7, O52 4/7, O59 7/7, O60 3/4, O60 4/4, O61 2/5(2), O61 4/5, O63 8/9, O64 2/7, O64 4/7, O64 7/7.
3. Less-altered basaltic material - samples O41 1/1, O54 1/1.

Table 2 Chemical compositions of substrates

Sample	← % →					← ppm →				
	Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb	Zn
O41 1/1	0.19	8.94	7.9	7.71	-	62	171	86	ND	129
O45 6/13	0.59	6.92	9.8	6.63	-	217	475	88	ND	237
O50 4/6	0.47	11.0	0.38	7.92	-	250	150	146	16	354
O51 2/7	0.27	10.81	0.60	6.26	3.00	337	188	84	ND	256
O51 3/7	0.95	9.58	1.79	6.92	-	710	590	176	19	359
O51 5/7	0.23	10.1	7.36	8.37	0.76	320	163	90	ND	240
O51 6/7	0.33	8.39	5.7	5.31	-	174	142	87	NS	168
O52 4/7	0.16	8.22	1.04	7.2	-	154	118	48	ND	166
O54 1/1	0.01	14.3	7.22	7.63	3.12	133	35	43	ND	210
O55 3/3	0.54	1.53	30.0	1.86	0.15	178	315	64	ND	72
O58 1/2	0.33	7.48	10.06	6.81	0.09	71	160	95	21	198
O58 2/2	1.51	7.82	10.3	5.97	-	166	118	427	34	296
O59 7/7a	0.42	10.61	1.64	6.12	1.93	624	270	71	26	480
O59 7/7b	0.91	7.75	5.67	6.55	0.21	305	370	205	40	170
O60 2/4	0.18	7.35	8.0	7.75	-	111	90	54	ND	183
O60 3/4	0.60	8.53	0.69	6.1	-	431	405	194	23	322
O60 4/4	0.40	7.99	0.67	8.23	2.38	371	320	132	12	282
O61 2/5a	0.35	2.84	22.0	3.03	0.12	480	460	-	19	185
O61 2/5b	0.69	5.94	17.64	6.42	0.09	738	600	134	18	317
O63 1/9A	1.41	2.77	23.0	3.31	-	853	1100	291	63	195
O63 1/9B	0.45	8.28	6.8	8.38	-	292	320	117	11	230
O63 5/9	0.35	0.35	31.8	0.62	-	138	320	54	17	61
O63 6/9	0.79	1.53	27.0	3.01	-	393	590	188	39	94
O63 8/9	1.76	8.61	1.96	7.50	-	640	970	399	44	363
O64 2/7	1.59	7.77	1.9	6.90	1.11	1169	815	369	39	328
O64 4/7	1.66	6.87	15.44	6.99	-	1059	1090	324	33	352
O64 5/7	0.77	5.65	19.9	3.83	0.12	146	460	147	45	120
O64 7/7	0.23	8.83	0.35	8.39	2.57	423	210	84	ND	381

TABLE 3 Mineralogy of substrates determined by x-ray diffraction

SAMPLE	SMECTITE	PHILLIPSITE	PLAGIOCLASE	PYROXENE	FRANCOLITE	OTHER
041 1/1	X	X	XXX	XXX		
045 6/13	XX	XX			XX	
050 4/6	X	XXX				Illite?
051 2/7	XX	XX				
051 3/7	XX	XXX				
051 5/7	X	XX			X	
051 6/7	XXX	X	?			Calcite
052 4/7	XX	XX	?			
054 1/1	X	X	XX	XX	X	
055 3/3					XXX	
058 1/2	X	XX	X	X	XX	
058 2/2					XX	Analcite
059 7/7 (1)	XX	XX				
059 7/7 (2)	X	XX	X	X	X	
060 2/4	XX		XX	X	X	
060 3/4	XX	XX				Calcite?
060 4/4	X	XXX				
061 2/5 (1)	X	X			XXX	
061 2/5 (2)	XX	XX			XX	
061 4/5	XX	XX				
062 3/3					XXX	Barite
063 1/9		X			XXX	
063 5/9					XXX	Barite
063 6/9A	X	X			XXX	
063 6/9B	XX		X		XX	
063 8/9	XX	XX				
064 2/7	XX	XX				
064 4/7	XX	X			X	
064 5/7	X				XX	
064 7/7	XX	XX				

XXX - dominant
 XX - important
 X - present

2.1.1 Francolite

Francolite (phosphorite) substrates are white, grey or yellow-white and are extremely friable (Plate 1). Phosphorites may form either by direct precipitation from upwelling waters of high biological productivity or by the phosphatisation of carbonates. Similar deposits to those found in the LI have been described from central and western Pacific seamounts by Hamilton and Rex (1959), Heezen et al. (1973) and Baturin et al. (1977). In each case these were phosphatised carbonates, and it is presumed that the LI phosphorites have a similar origin.

Francolite was identified at depths between 1,400 m + 3,850 m. No evidence of replacement by ferromanganese oxides was observed, although oxide penetration along planes of weakness was noted (Plate 1). Barite was positively identified in two substrates (062 3/3, 063 5/9).

2.1.2 Phillipsite/smectite

Substrates showing only these two minerals in x-ray diffractograms are those most commonly found. Since these minerals are well known weathering products of basaltic glass (e.g. Rex 1967), phillipsite/smectite substrates are likely to represent highly weathered basaltic rocks. Their morphology is variable, in part according to the relative abundance of the two components. Substrate 050 4/6 (Plate 2) is rust-coloured, extremely friable and comprises needle-like particles visible to the naked eye. These are revealed by XRD to be phillipsite. The dredge description (Appendix 1) indicates that the contents are volcanoclastic sandstones, some graded, suggesting derivation from turbidity currents.

The most common morphology is a thin, buff-coloured honeycomb of brittle material infilled with extremely friable, rust or fawn-coloured material (Plate 3). Such a morphology is exhibited by 051 2/7, 051 3/7, 059 7/7, 060 3/4, 061 2/5 and 064 7/7. Although mineralogical identification has not been made of the separate phases,



Plate 1. Sample O64 4/7. Francolite substrate. Fe-Mn oxide penetration has occurred along planes of weakness. The surface of the crust has a botryoidal morphology.



Plate 2. Sample O50 4/6. Phillipsite substrate (Zone S), showing probable replacement by Fe-Mn oxide (Zone B). The crust exhibits laminations on a millimetre scale, and has a smooth upper surface. Scale as in Plate 1.

the similarity of colour and texture between the friable material and the phillipsite of O50 4/6 suggests that it is phillipsite and thus that the brittle honeycomb comprises smectite. The cell dimensions of the honeycomb vary from 2-10 nm, possibly reflecting the coarseness of the original rock. The patches of redder material may represent weathered Fe-rich olivine phenocrysts (Plate 3).

Although the highly weathered nature of the substrates precludes identification of the parent rock, similar material has been described by MacDonald (1954) from Bikini Atoll and by Rex (1967) from Sylvania Guyot. Incompletely altered fragments led both these authors to suggest that the original material was a tuff breccia.

With increasing smectite content the substrate becomes powdery and pale-fawn in colour (O51 6/7). The Fe content of O51 6/7 is high (8.4%) + similar to substrates rich in phillipsite and redder in colour. Rex (1967) has identified a chloritic, mixed layer clay consisting of montmorillonite with interlayer ferric hydroxide in similarly weathered basalt. Mineralogical identification of the <0.5 μm fraction of O51 6/7 suggests that it is composed of pure smectite. Thus whilst some of the Fe may be present as interlayer Fe (III) hydroxide, most is likely to occur within the smectite lattice.

The phillipsite/smectite substrates contain 6-8% Al, 8-14% Fe and 0.2-0.6% Mn, yielding Mn/Fe ratios of 0.02-0.1. Cu, Ni and Zn contents are between 100 and 500 ppm, Co and Pb less than 100 ppm. These values are 2-4 times greater than less weathered material (O41 1/1, O54 1/1), possibly as a result of trace metal adsorption by Fe oxides from seawater penetrating the friable substrate.

2.1.3 Less altered basaltic material

Dredge reports (Appendix 1) suggest that the dominant rock type in the region is alkali olivine basalt with a clinopyroxene - plagioclase - olivine mineralogy. Whilst olivine was not identified in any substrate, plagioclase + pyroxene were found in O41 1/1, O54 1/1, O58 1/2, O59 7/7(2)



Plate 3. Sample 051 3/7. Substrate comprises a honey-comb of smectite infilled with phillipsite. Scale as in Plate 1.



Plate 4. Sample 062 3/3, showing a nodule morphology.

and O60 2/4; O41 1/1 and O54 1/1 are particularly rich in these minerals. O41 1/1 + O60 2/4 are vesicular and are altered, as revealed by their variegated nature and the lack of olivine. Furthermore, phillipsite and smectite are observed in O41 1/1. Vesicles are typically .5 - 1 mm in diameter. O54 1/1 is non-vesicular and varies between brown and dark green in colour.

2.1.4 Mixed substrates

The juxtaposition in several substrates (O45 6/13, O51 5/7, O58 1/2, O61 2/5, O63 6/9A, O63 6/9B) of francolite, phillipsite and smectite is indicative of crust development on debris slopes. Overall, it is clear that ferromanganese crusts develop on any stable substrate.

2.2 Crust description

The salient points of crust morphology are discussed below:-

1. Thickness - thickness of the crusts varies from 1-70 mm, with a mean of 20 mm (Appendix 1). Most are less than 30 mm.

Since the LIA developed synchronously along its length (Jackson and Schlanger 1976), no simple relation between position and crust thickness is seen, in contrast to the Hawaiian Archipelago (Craig et al. 1982). Further, there is insufficient age data of individual seamounts to determine any possible relation between thickness and age. Assuming the LI crusts have developed at 1 mm my^{-1} , apparently typical of encrustations (Ku et al. 1982), it is interesting to note that few crusts thicker than 30 mm have been dredged on an archipelago 70 my old. This may be interpreted as being due to crust development on more recently formed talus slopes.

2. Shape - almost all the LI samples are encrustations rather than nodules - i.e. they form a continuous rind over large blocks or rock outcrops. Only O62 3/3 shows clear indications of grading into a nodule morphology

(Plate 4). On a larger scale, it is impossible in the absence of bottom photographs to ascertain the lateral relations of the encrusting Fe-Mn material.

For thin crusts, shape is dictated by the surface shape of the substrate (Plate 3), whilst thicker crusts (>1 cm) tend to be smoother (Plate 2). An undulating surface unrelated to the substrate but due to the botryoidal growth habit of Fe-Mn oxides is seen in some cases (Plate 1).

3. Surface texture - most commonly, the crusts exhibit a combination of smooth and microgranular surface textures. Moorby (1978) has observed the same textural combination on some nodules from the Indian Ocean and has pointed out that higher relief granules occurred in protected hollows, suggesting that a smooth texture may result from abrasion by a moving nepheloid layer. The same relationship is found in the crusts and may be explained by the same phenomenon in view of the more rapid currents in the upper ocean. Abrasion may also occur during the dredging process, but this may usually be discerned by the freshness of resulting fractures and surface features.

Crusts 045 6/13, 058 2/2, 061 4/5 and 064 4/7 have botryoidal surfaces (Plate 1). The botryoids are elongated horizontally, are 0.5 - 2 cm across and 0.3 - 0.8 cm in height. The botryoids are sparse, in contrast to the tightly packed botryoids of some Hawaiian crusts (Glasby and Andrews, 1977).

Finally, in some cases worm casts are seen on the crust surfaces, indicative of benthic activity.

4. Internal structure - on a macroscopic scale, the crusts show much less variety than do nodules. The constant mineralogy of the crusts (see Section 3.1) precludes mineralogical zoning and the generally low aluminosilicate content precludes pronounced layering due to variations in detrital mineral abundance.

The distinct boundary between crusts and substrates allied to the general lack of increase in the detrital mineral content of the crusts towards the substrate boundary

suggests that replacement of the latter by the former is a slow process, although penetration along lines of weakness is common (Plate 1). In O5O 4/6 and O61 4/5B total replacement of part of the substrate may have occurred. This is inferred from the higher detrital mineral content of that part of the crust nearest to the substrate (Plate 2).

Indistinct layering on a centimetre scale is evinced both by variations in the detrital mineral content or by poorly defined discontinuities (Plates 2 & 5). The cause of the discontinuities is not clear. Sampling across the discontinuities revealed no significant chemical variations (Section 4.2). In some cases they are pinched out by clay partings, which suggests that they may represent periods of non-growth. Occasionally millimetre - scale laminations occur (Plate 2).

2.3 Sampling Procedures

59 oxide samples were taken from 16 stations. Samples were taken from different crusts from the same station to examine within-station variability. Individual layers within crusts were sampled, either by hand separation or using a small steel drill. For crusts of sufficient thickness, more than one sample was taken in order to examine within-crust variability. For very thin crusts it was not always possible to completely separate oxide material from substrate material, leading to contamination of the crust sample.

CHAPTER 3 MINERALOGY AND BULK GEOCHEMISTRY

3.1 Mineralogy

The mineralogy of the ferromanganese oxide crusts was determined by X-ray diffractometry. Samples were finely ground in an agate pestle and mortar and mounted as smear mounts. XRD traces were made using a Phillips X-ray generator, goniometer and pulse height analyser. The samples were subjected to Fe $K\alpha$ radiation (34 kV, 28 mA) during $1^\circ 2\theta \text{ min}^{-1}$ scans from $5-90^\circ 2\theta$.

Todorokite, birnessite + δMnO_2 (Z - disordered manganate, Arrhenius et al. 1979) are the Mn oxide minerals commonly found in ferromanganese nodules. In all but one crust (O53) δMnO_2 was the sole Mn oxide identified, on the basis of broad and weak peaks at 2.4 and $1.4\overset{\circ}{\text{Å}}$. In most cases the $2.4\overset{\circ}{\text{Å}}$ peak is sharper than the $1.4\overset{\circ}{\text{Å}}$ peak, which is often absent. A typical XRD trace of the crusts is shown in Fig. 2. No relation was noted between the crystallinity of the δMnO_2 and the thickness of the crusts, the Mn content or the Mn/Fe ratio. Diagenetic changes within the crusts, if any, do not appear to affect the Mn oxide mineralogy, which must therefore be determined before or soon after the accumulation of the oxides at the surface of the crusts.

Todorokite was identified in crust O53 by the presence of weak $9.8\overset{\circ}{\text{Å}}$ peaks. Confirmation that the peak was due to a Mn oxide was made following X-ray diffraction of residues from samples leached with acidified hydroxylamine hydrochloride, which destroys Mn oxides. It is interesting to note that O53 was from particularly deep water (4,700 m), has a very high Al content (6%) and comprises an intimate mixture of phillipsite and Mn-Fe oxides. It therefore more resembles an oxide - enriched indurated sediment than a true encrustation.

The occurrence of δMnO_2 as the dominant Mn oxide mineral confirms and extends the findings of Cronan (1977), Friedrich and Schmitz-Wiechowski (1980) and Craig et al.

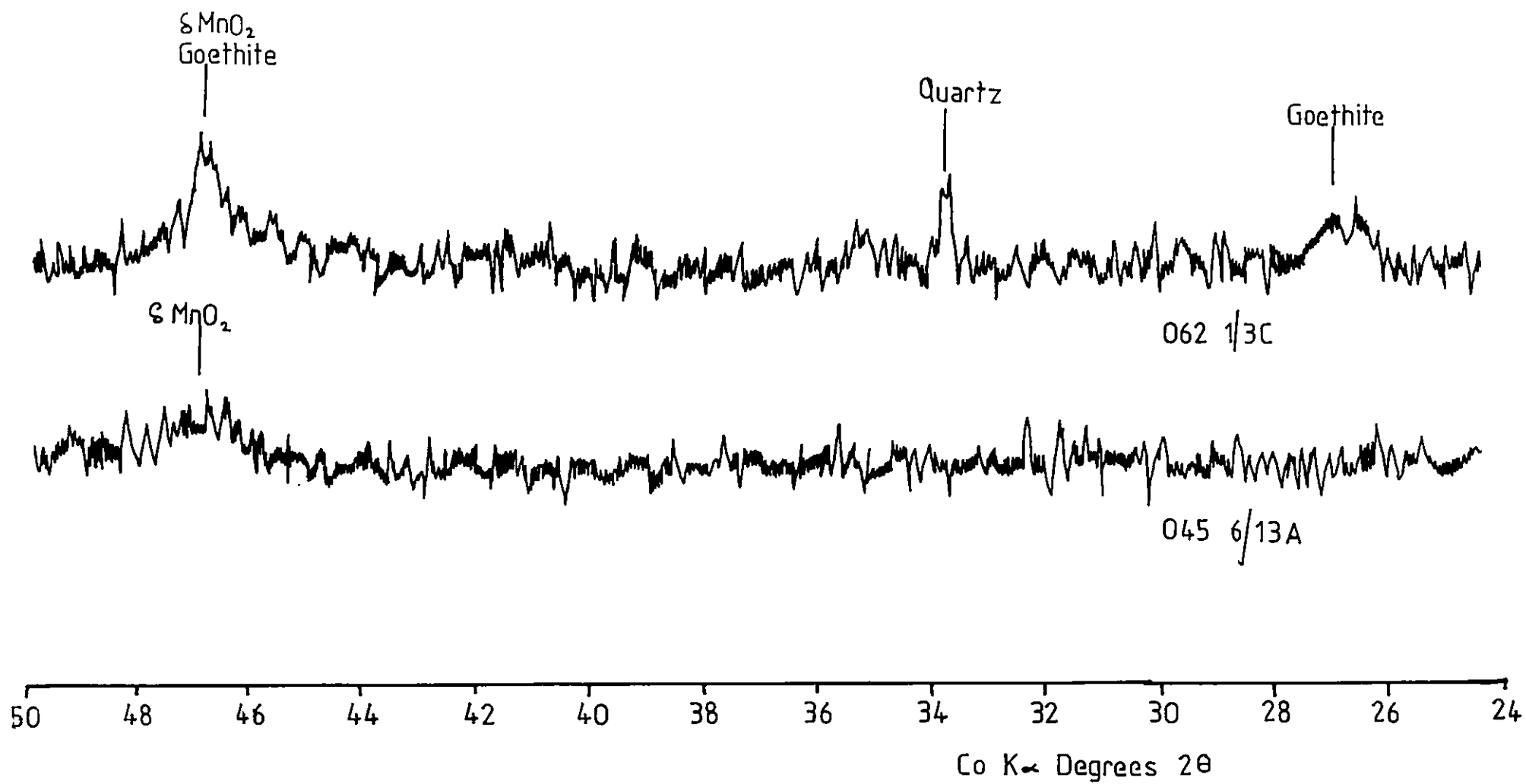


Fig 2. X-ray diffractograms of ferromanganese crusts 062 1/3C and 045 6/13A.

(1982) concerning the mineralogy of seamount nodules and encrustations. It has been suggested (Meylan and Goodell 1976, Halbach et al. 1984) that todorokite forms in nodules where the Mn/Fe ratio exceeds about 2-2.5. In the crusts, however, SMnO_2 occurs in all samples, even when the Mn/Fe ratio approaches 4.0 (Craig et al. 1982, this work).

The Fe oxide phase of marine ferromanganese deposits is commonly considered to be a disordered Fe oxyhydroxide ($\text{FeOOH} \cdot x\text{H}_2\text{O}$, Burns and Burns 1977) and is probably related to their fine-grained nature. This is the case for almost all the LI samples; only in samples O62 1/3C and O62 1/3D was a crystalline Fe oxide, goethite, positively identified by means of a broad, weak peak at $4.16\text{\AA}$ and an enhancement of the $2.45\text{\AA}$ SMnO_2 peak (Fig. 2). Goethite may also be present in samples O62 1/3E and O62 1/3F.

Quartz was identified in almost all samples, and plagioclase, phillipsite, francolite and halite in a certain number. Such accessory minerals may be incorporated into the crusts by settling through the water column or by oxide replacement of associated substrates.

3.2 Bulk geochemistry

Chemical compositions of the crusts were determined by two methods. Firstly, analysis for Mn, Fe, Cu, Ni, Co, Pb, Zn, Ca, Al + Ti was carried out by atomic absorption spectrophotometry (AAS) and secondly the above 10 elements plus Li, Be, Cr, Na, K, Mg, P, Sr, Ba, Mo, La, V, Ag and Cd were determined by inductively coupled plasma spectrophotometry (ICP). Thirdly, rare earth element (REE) determinations were carried out on selected samples on the King's College ICP. Analytical techniques are described in Appendix 3, and Appendix 3 discusses the precision and accuracy of the determinations.

Comparison of the AAS + ICP data suites indicates that interference effects associated with the high Mn + Fe content of the material reduces the level of accuracy

on the ICP. Generally, concentrations of both major and trace elements were depressed by 5-20% on ICP with respect to AAS. Because we have little idea whether or not the 14 elements determined solely by ICP will be similarly affected, no corrections to the data may be made. The precision of the data is, however, good. In addition, almost no previous determinations of these elements have been made on similar material. The entire data set is shown in Appendix 4 and the mean abundances in Table 4 together with data for hydrothermal Mn crusts, Pacific Ocean nodules + 8MnO_2 -rich nodules.

3.2.1. Comparison with hydrothermal Mn crusts

Over the past ten years many discoveries have been made of Fe-rich and Mn-rich encrustations associated with hydrothermal activity on the mid-ocean ridge system (Scott et al. 1974, Moore and Vogt 1976, Corliss et al. 1978, Toth 1980) and recently in a volcanic arc setting (Cronan et al., 1982). These deposits are characterised by accumulation rates 2 or 3 orders of magnitude greater than abyssal nodules, by low trace metal contents and by extreme Mn/Fe ratios (Scott et al. 1974, Moore and Vogt, 1976). The mineralogy of the Mn-rich crusts is usually well-crystalline birnessite or todorokite (Moore and Vogt, 1976, Corliss et al. 1978, Cronan et al. 1982).

The LI crusts show no evidence of hydrothermal influence. Their mean Mn/Fe ratio approaches unity, in contrast to the hydrothermal ratios which are typically greater than 45. Most trace elements are 1-2 orders of magnitude more abundant in the LI crusts. Taking encrustations from the Galapagos Mounds hydrothermal field to represent a typical hydrothermal crust, then enrichment factors for the LI crusts over the hydrothermal crusts are:-

Li	0.06	Cu	16
Mo	0.8	Pb	16
Sr	2	Ni	26
V	5	Ti	52
Zn	5	Co	360

Table 4 Mean chemical compositions of LI crusts and other Fe-Mn oxides

Element Sample	K* ⁵	Na*	Mg*	Ca	Al	Mn	Fe	Li*	Sr*	P*	Ti	V*	Mo*
LI crusts (59) ¹	0.64	-	1.06	2.59	1.56	20.4	17.0	5.0	1190	3880	12000	530	420
Galapagos hydrothermal mounds Mn crust ²	0.65	-	1.6	1.1	0.63	44.0	0.93	83	660	1190	230	108	510
Penrhyn (23) Basin + Phoenix Is. SMnO ₂ nodules	-	-	-	1.9	2.3	17.7	17.0	-	-	-	13000	-	-
Hydrogenus Mn nodules, Pacific ⁴	0.75	-	1.71	2.0	3.06	19.8	12.0	-	850	2350	6700	530	440

¹ No. of samples

² from Moorby + Cronan, Initial Reports DSDP 70, in press

³ this work

⁴ from Cronan (1976)

⁵ asterix marks ICP determined elements

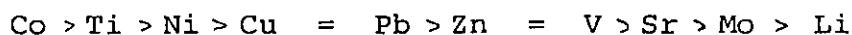
K, Na, Mg, Ca, Al, Mn, Fe - weight %

all other elements in ppm

Table 4 (Cont.)

Element Sample	Co	Ni	Cu	Zn	Ba*	Pb	Ag*	Cd*	Cr*	Be*	Mn/ Fe
L.I. Crusts (59)	5450	3860	1540	590	1370	1020	5.0	4.0	37.1	5.36	1.2
Galapagos hydrothermal mounds Mn crust	15	150	94	108	-	64	-	-	-	-	47
Penrhyn Basin + Phoenix Is. SMnO ₂ nodules (23)	3440	3370	2200	560	-	910	-	-	-	-	1.0
Pacific hydrogenous nodules	3400	6300	3900	680	2800	850	6	7	13	-	1.7

The enrichment sequence for the LI crusts over the Galapagos crust is thus:-



Since the hydrothermal crusts accrete very quickly and have little time in which to accumulate trace metals from the water column, the enrichment sequence may represent the ratio of the affinity of Fe and Mn oxides for trace metals over the hydrothermal supply of that element.

The lack of discernable hydrothermal influence in the LI crusts is no surprise. The majority of the volcanism in the chain ended 65 My BP, and even the most recent K-Ar date for late-stage volcanism is 44 My BP (Garcia, pers. comm. 1982). Using a growth rate of 2 mm My^{-1} , similar to that assumed by Craig et al. (1982) for Hawaiian Archipelago crusts, even the thickest crust will have developed in the last 35 My, well after the cessation of volcanism. Most crusts are much more recent and have developed either on heavily weathered pyroclastic rubble or phosphatised limestone. The state of weathering of the rubble suggests it has been exposed to seawater for tens of millions of years (Rex 1967) and will to a large extent be in chemical equilibrium with seawater.

3.2.2. Comparison with abyssal Pacific nodules

The compositional diversity of Pacific nodules allow only a general comparison to be made between them and the LI crusts.

In recent years it has become clear that the composition of most abyssal nodules may be interpreted in terms of metal accumulation from 2 sources-seawater and interstitial water. Early diagenetic reactions in the sediment affect the composition of the interstitial waters and thus the composition of nodules developing from the waters (Lyle et al. 1977, Calvert and Price 1977, Klinkhammer 1980). Nodules affected by diagenetic reactions in associated sediment tend to be enriched in todorokite, Mn, Cu, Ni + Zn and have higher Mn/Fe ratios than SMnO_2 -rich nodules,

which are enriched in Co, Pb + Ti (Cronan 1980). Since the LI crusts are accreting from seawater only, differences in the composition of nodules and crusts within ocean provinces will largely reflect element supply from associated sediment. The mean Pacific nodule (Table 4) reflects nodules which have a diagenetic component, and comparison of the nodule and the crusts reflect this in that the crusts are depleted in Ni, Cu, Zn, Ba + Cd and are enriched in Fe, Ti, Sr, Co + Pb. Mo + V contents are similar. It is interesting to note that the difference in the Mn/Fe ratio is due to a lower Fe content in the nodules, whilst the mean Mn contents are similar.

3.2.3 Comparison with 8MnO_2 -rich nodules

Comparison of the crusts with 8MnO_2 -rich nodules from the close-by Penrhyn Basin minimizes chemical differences which may be due to a regional variation in element supply + to mineralogical differences. The bulk chemistry of each is very similar; Mn + Co are, on average, enriched in the crusts, whilst Cu is slightly depleted. Fe, Ti, Ni, Zn + Pb are present in similar amounts in both sample groups. The greater abundance of Al in the nodules is interpreted as being due to a greater incorporation of aluminosilicates from associated sediment.

Clearly there is a strong relationship between the crusts and the 8MnO_2 -rich nodules, which is discussed in greater detail in Chapter 12 on nodule geochemistry.

3.3 Inter-element associations - correlation analysis

Linear correlation analysis has been used extensively to establish element associations in Fe-Mn nodules. Associations have been derived from both bulk chemical data (Goldberg 1954, Riley and Sinhaseni 1958, Willis and Ahrens 1962, Cronan and Tooms 1969, Calvert and Price 1977) and from electron probe data (Burns and Fuerstenau 1966, Aumento et al. 1968, Cronan and Tooms 1969, Friedrich

et al. 1969, Moore et al. 1981. More recently inter-element correlations from some Fe-Mn encrustations have been published (Colley et al. 1979, Friedrich + Schmitz-Wiechowski 1980, Craig et al. 1982). These results are summarised in Table 5.

Caution must be exerted in the interpretation of correlation matrices. Firstly, the condition that the sample population be normally distributed is not met in most geological samples; many elements show a log-normal distribution. This may be overcome by log-transforming the data. In this case, however, transformation had little effect on the observed correlation coefficients. It is nevertheless important to examine correlation matrices in conjunction with element scatter plots (Figs. 3-19), since the latter reveal the presence of outliers which can markedly affect observed correlation coefficients (r), in addition to separating populations within the whole.

Secondly, it should be kept in mind that explained variation is defined by r^2 . For example, when $N > 60$, $r = 0.4$ is significant at the 99.9% confidence level, yet only 16% of the variation of that element is explicable by its association with the second, at that level of correlation.

3.3.1 Bulk data correlation

Correlation data for elements with the main phases in the crusts is shown in Table 6, which yields information on the distribution of elements between aluminosilicate and authigenic oxide phases.

In a suite of samples with widely different Al contents a strong positive correlation with Al indicates that an element is contained dominantly within the aluminosilicate fraction. For the crusts this is seen to be the case for Li + K, and to a lesser extent for Na, Cr + Cu. Li, K, Na + Cr are well known lithophile elements.

Table 5 A summary of metal correlations in ferromanganese
nodules and crusts

<u>Nodules</u>	<u>Correlations</u>
1. Goldberg (1954)	Fe-Co-Ti-Zr; Mn-Ni-Cu
2. Willis and Ahrens (1962)	Ni-Cu; Fe-Co
3. Burns and Fuerstenau (1966)	Fe-Co-Ti-Ca Mn-Cu-Ni-Zn-Mg-K-Ba-Al
4. Barnes (1967)	Pb-Co; Co- 8MnO_2
5. Cronan (1967)	Fe-Ti- H_2O ; Cr-detrital
6. Cronan (1969)	Mn-Ni-Cu-Mo; Co-Pb
7. Calvert and Price (1970)	Mn-Ba-Co-Ni-Si-Mo Fe-As-Pb-Y-Zn-P
8. Calvert and Price (1977)	Mn-Mg-Ba-Cu-Mo-Ni-Zn Fe-Ti-P-As-Pb-Sr-Y-Zr

Crusts

1. Aumento et al. (1968)	Mn-Co-Ni
2. Colley et al. (1979)	Mn-Co-Ni-Cd-Pb
3. Friedrich + Schmitz- Wiechowski (1980)	Mn-Co-Ni
4. Craig et al. (1982)	Mn-Co-Ni

Table 6 Correlation data for the major phases in the
complete sample suite

N = 59

Only values significant at the 99.9% confidence
level ($r = 0.40$) are quoted

r	Mn	Fe	Al	Na
1.0				
0.9			K Li	
	Mo Co			
0.8	Sr			
0.7	Cd V	Sr V		
0.6	Ag Pb Ni	La Ti Be		Mg K
0.5	Zn Ti		Na Cr Cu	Li Al
0.4				
-0.4				Ba Mo
-0.5		Na	La Cd Zn Ti	Pb Ni Ti
-0.6	Na		Ag Co Pb	Sr Zn V
-0.7	Li K	Li K	Mo	
-0.8	Al		V	
-0.9			Sr	
-1.0				

Na also correlates significantly with Mg. This is thought to be due to the presence of seasalt.

Conversely, a strong negative correlation with Al + a positive correlation with Mn and/or Fe are indicative of oxide related elements. This is the case for Mn, Fe, Co, Ni, Pb, Zn, Mo, V, Ag, Cd, Sr, Ti and Be. The presence of Be in this phase is interesting, since it is generally thought of as a lithophile element (Li 1982). 2 explanations may be forwarded:-

1. That ppm concentrations of Be are associated with Fe + Mn flocs in seawater,
2. That the dominant aluminosilicate assemblage of the crusts is phillipsite-smectite, which are weathering products of basalt. Be (+ Ti, which is also commonly associated with Al) may have been leached during this process, precluding a strong Be-Al correlation. However, in the absence of Be data for the substrates, this hypothesis cannot be tested.

3.3.2 Oxide phase inter-element associations

Although the occurrence of aluminosilicate/francolite impurities are of great importance to overall element content and variance, their presence inhibits observations on the oxide phases. A new data set was therefore created omitting samples significantly contaminated with francolite or aluminosilicate. The criteria for omission were:-

1. Ca content > 3%. Uncontaminated crusts exhibit a very constant Ca content of 2-2.5%, enabling contamination to be easily detected.
2. Al content > 1.5%. This level is much more arbitrary than the 3% Ca level, since Al varies more than Ca. However, since the Mn + Fe content of the crusts, representing the oxide phase, only starts to drop off significantly above this level, it can be assumed that contamination is small at lower Al contents. The resulting correlation matrix is shown in Table 7.

Table 7 Correlation data for the major phases in the
sample set with aluminosilicate or francolite
contaminated samples omitted (see text for
details)

N = 40

Only values significant at the 99.9% confidence
level are quoted ($r = 0.50$)

r	Mn	Fe	Al
1.0			
0.9	Ni		
	Co		
0.8	Cd		
0.7			
	Mo, Ca		Cu
0.6			
			Li, K
0.5			
			Be
-0.5			
-0.6	Fe	Mg	Ni
		Co	
-0.7	Al	Cd	Cd
		Ni	
-0.8			
-0.9			
-1.0			

Comparison of Tables 6 & 7 shows that the correlation coefficients between many trace elements and Mn and Fe change radically once the francolite/aluminosilicate impurities are removed. Some general rules may be drawn up to explain the changes:-

1. If a trace element is associated almost exclusively with one major element, its correlation coefficient with that element is strongly positive in all data sets. This is the case for Li + K, with Al, and for Co, Cd and to a lesser extent Mo, with Mn.
2. If a trace element is contained in the oxide fraction, but is partitioned between the Mn and Fe phases, it exhibits a negative correlation with Al and a positive correlation with both Mn and Fe in the bulk data matrix, and less positive correlations with Mn and Fe in the contaminant-free subsets. Precise correlations in the subsets depend on the relative affinity of the element to 5MnO_2 , $\text{FeOOH} \cdot \text{H}_2\text{O}$ + goethite.

This is best illustrated with reference to Sr and Ti. As can be seen from the raw data set, both elements are contained dominantly in the oxide phases. However, their weak correlations with Mn and Fe in the oxide subset indicate no particular affinity for either Mn or Fe oxides.

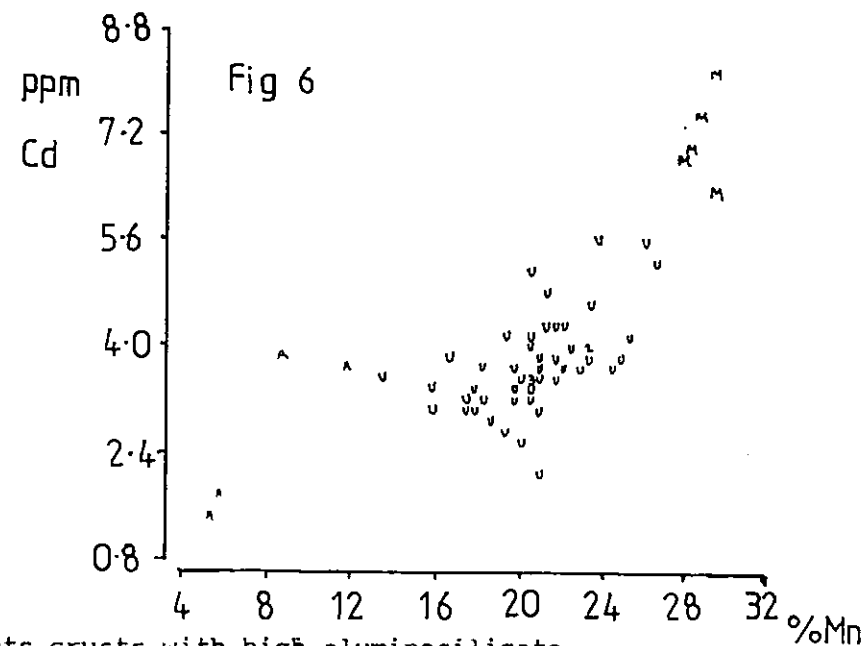
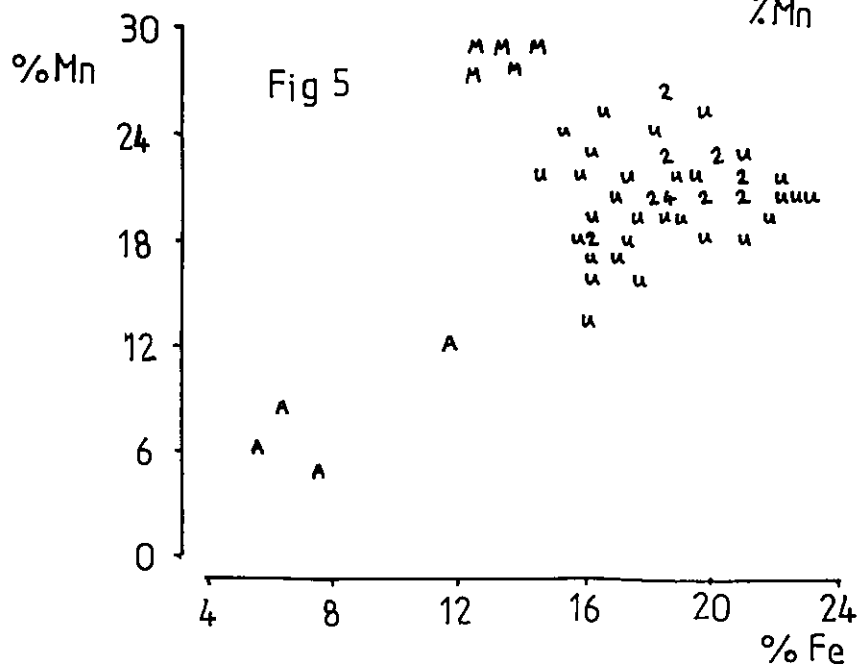
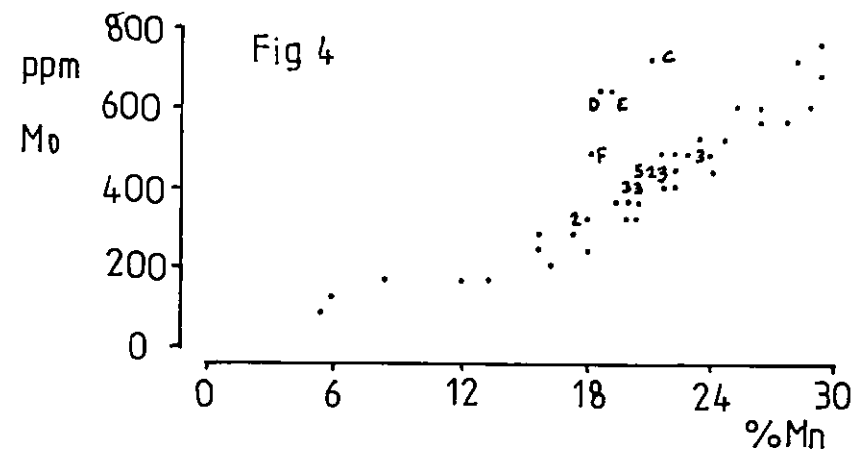
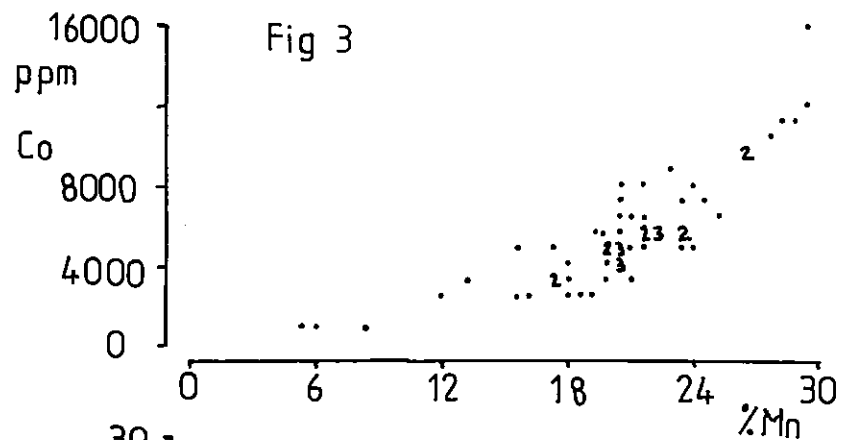
Particularly strong associations can be seen between the elements Al-K-Li-Na, a well-known aluminosilicate association, and Mn-Mo-Co, which are 5MnO_2 -associated (Figs. 3 + 4). In addition, a modest correlation is noted between Na and Mg, probably due to the presence of seasalt.

Weaker associations may be elucidated most clearly by simultaneous consideration of the correlation matrices and scatter plots. A plot of Mn versus Fe (Fig. 5) reveals 3 sample populations:-

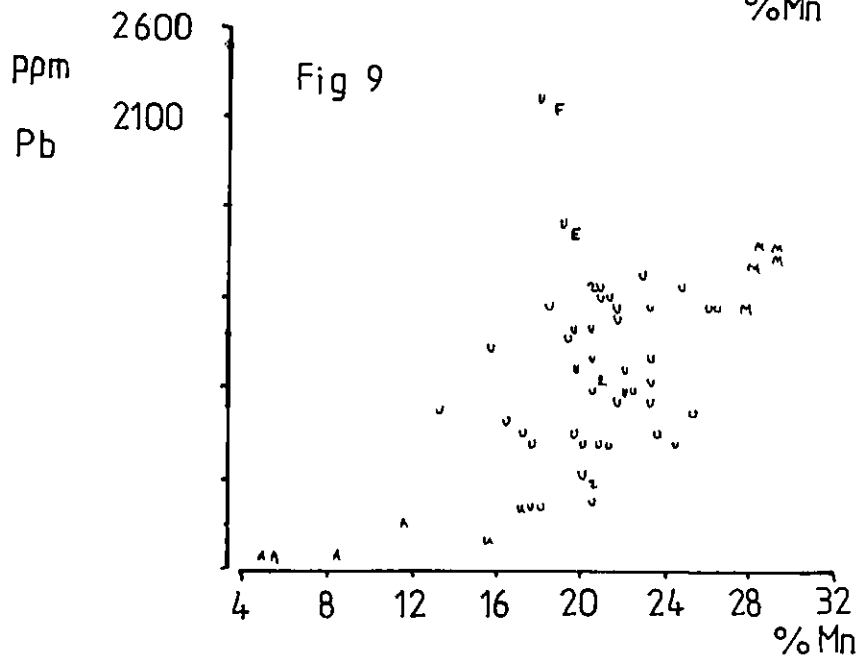
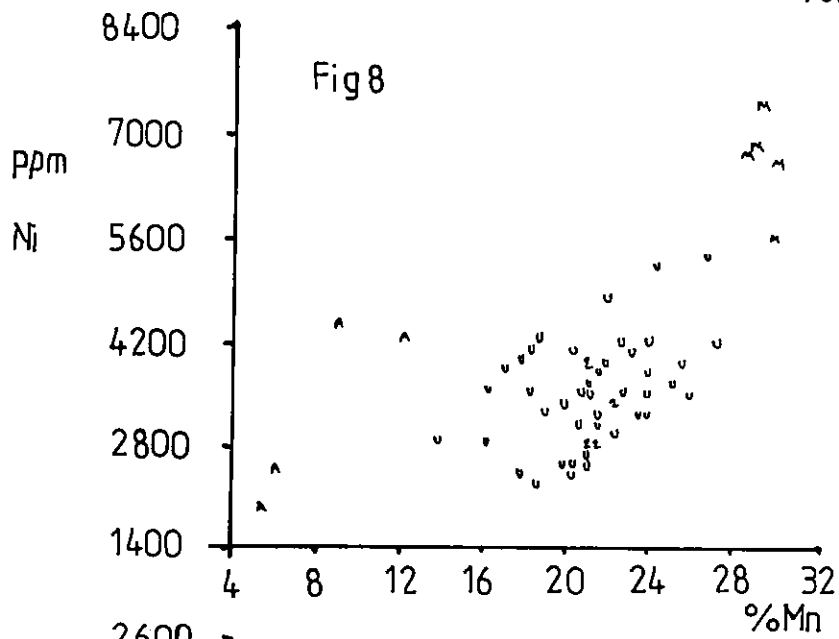
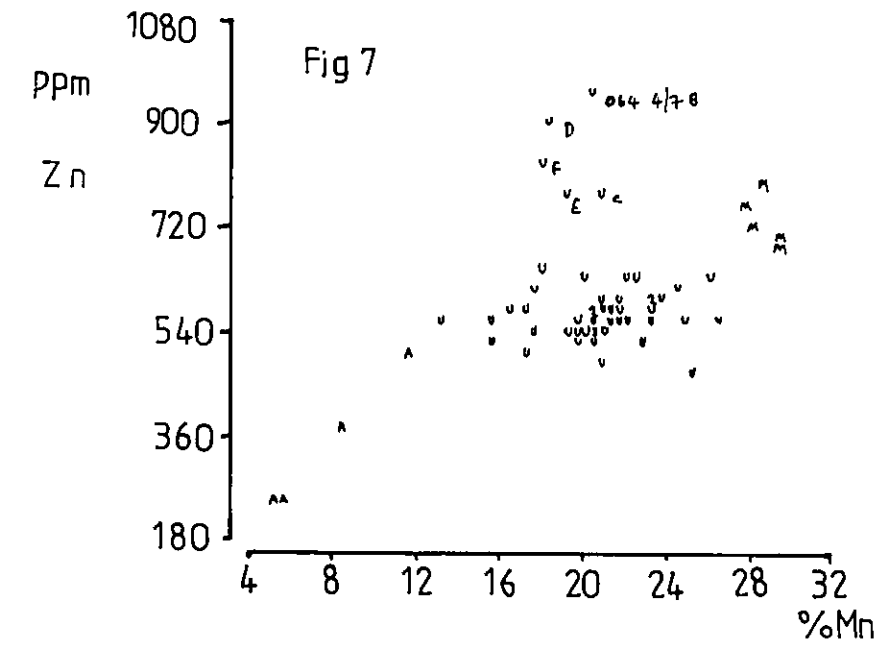
Group 1 - high aluminosilicate, low Mn and Fe (4 samples, signified by 'A').

Group 2 - Mn and Fe present in similar abundances (signified by 'U').

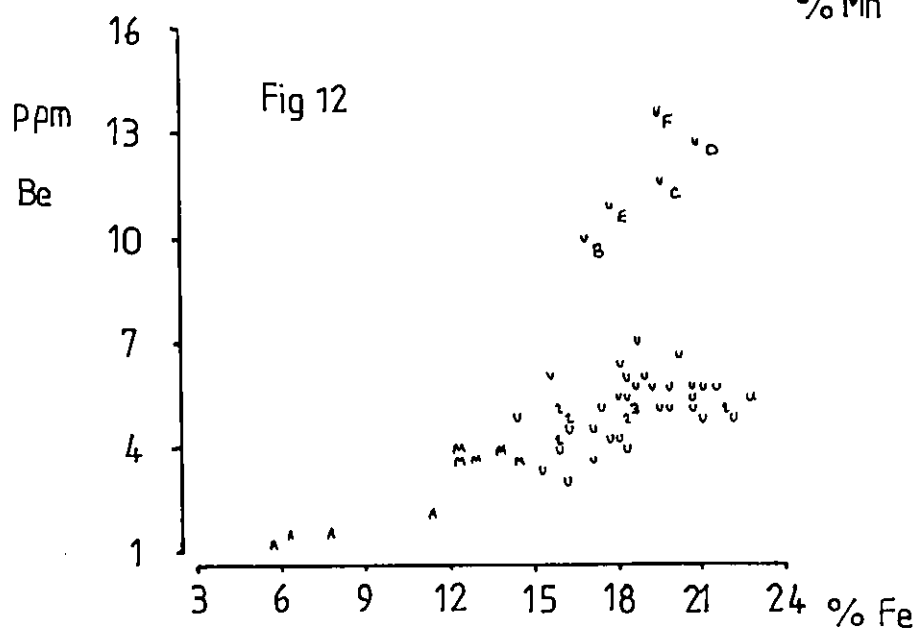
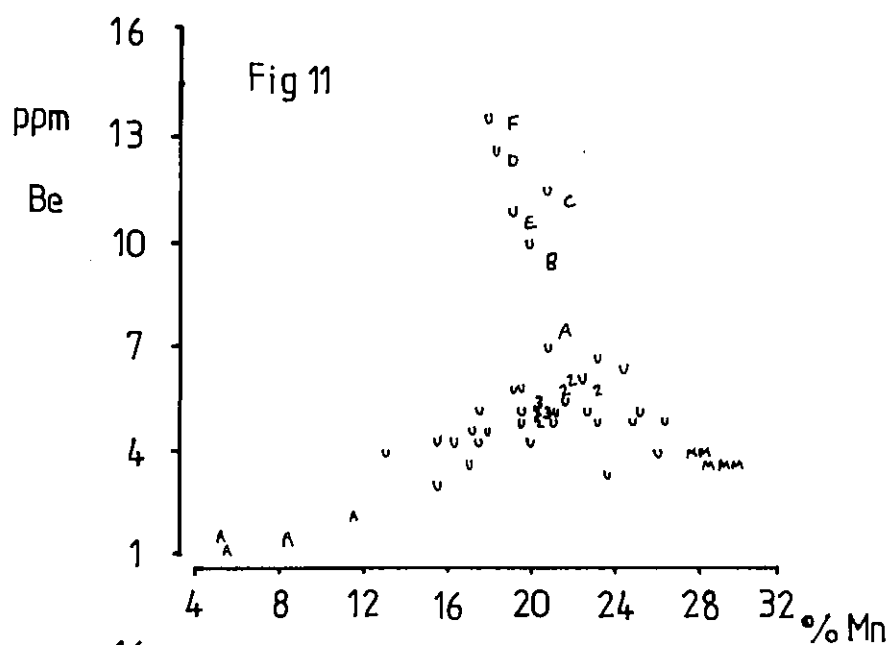
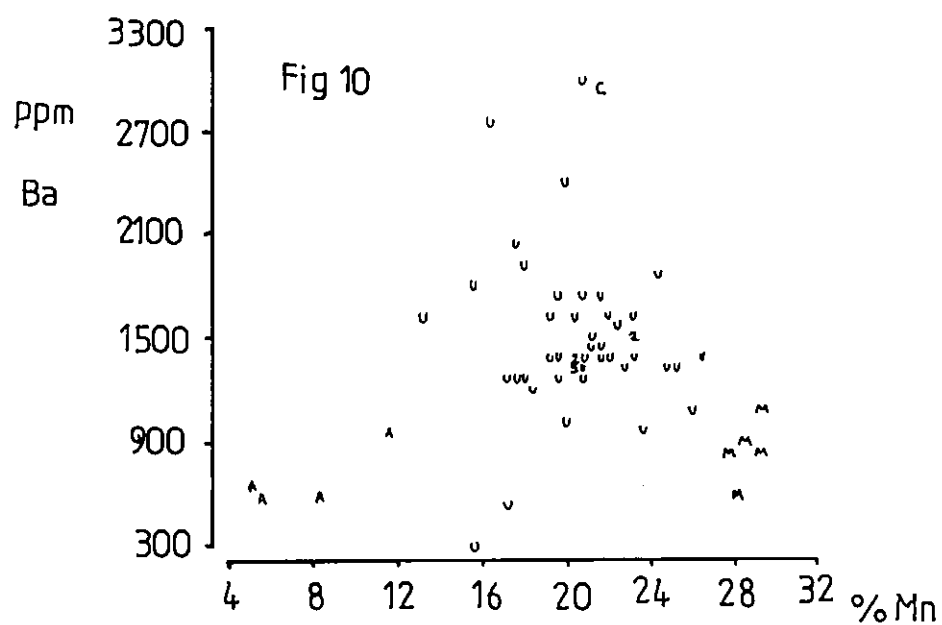
Group 3 - enhanced Mn contents, decreased Fe contents (5 samples, signified by M).



Figs. 3-19. Element associations in the LI crusts. A represents crusts with high aluminosilicate contents, U represents crusts with Mn/Fe ratios close to unity, M represents crusts with high Mn/Fe ratios (see section 3.3.2). A-F represent samples from crust 062 1/3. Numbers represent more than one data point.

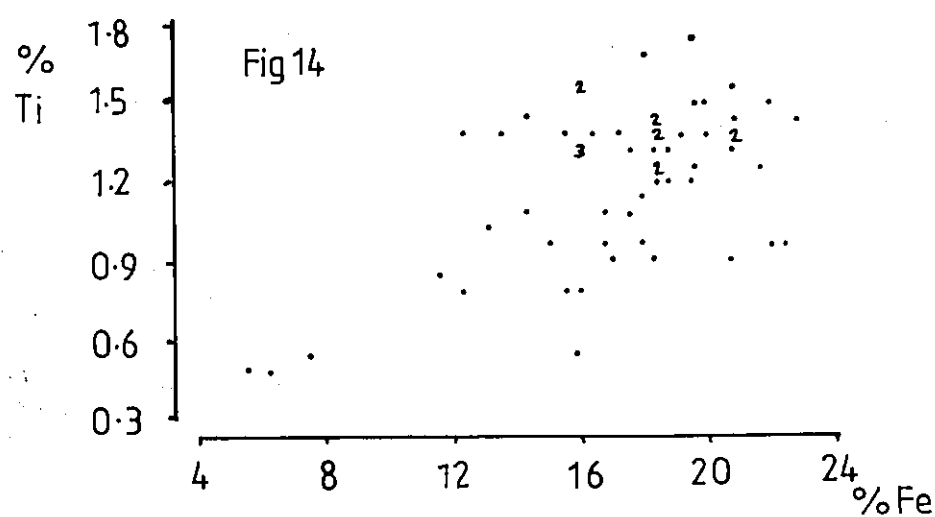
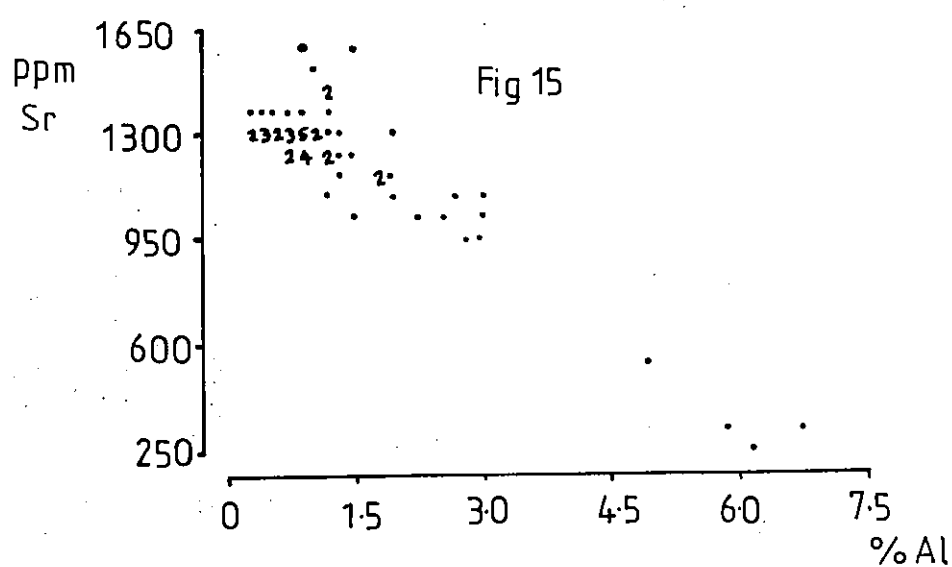
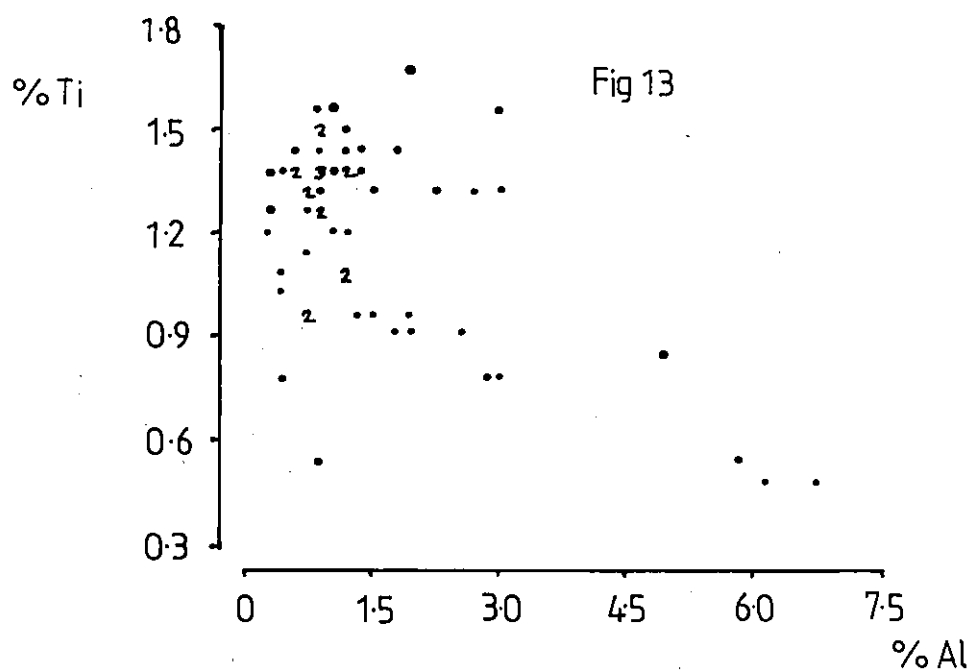


Figs. 7-9. Element scatter plots for the LI crusts. See Fig.3 for legend.



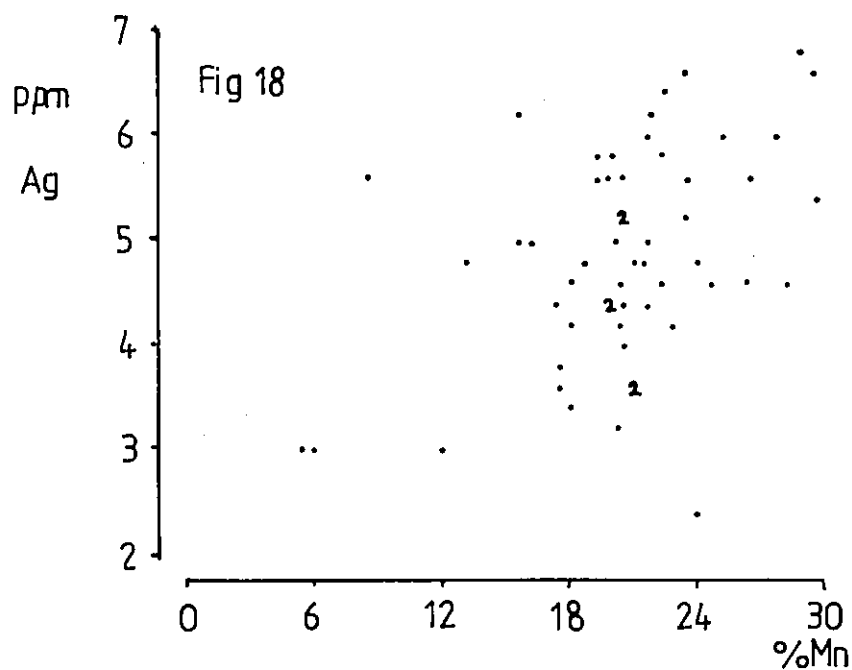
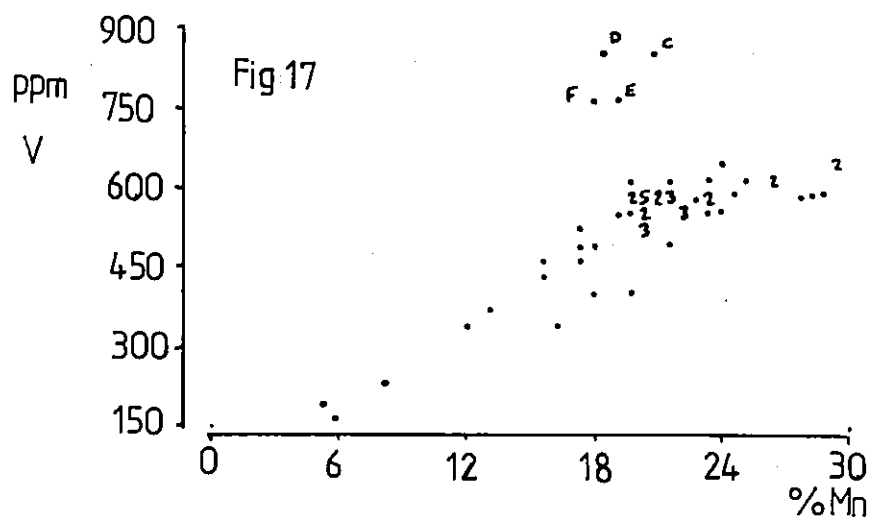
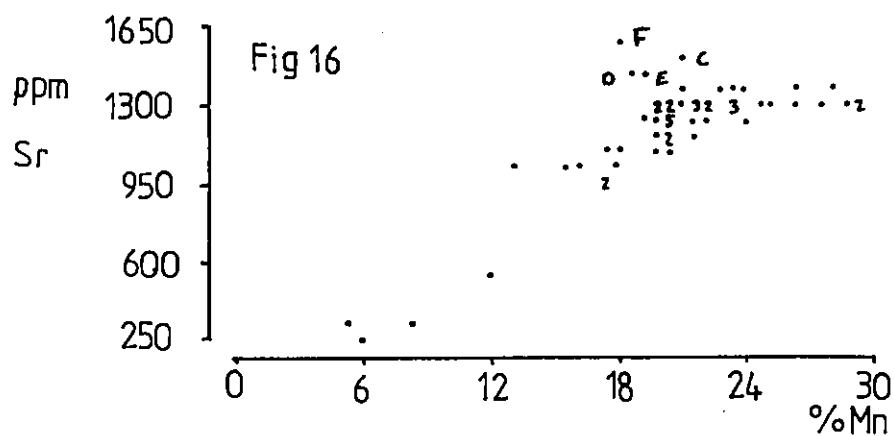
Figs. 10-12. Element scatter plots for the LI crusts.

See Fig.3 for legend.



Figs. 13-15. Element scatter plots for the LI crusts.

See Fig. 3 for legend.



Figs. 16-18. Element scatter plots for the LI crusts.

See Fig.3 for legend.

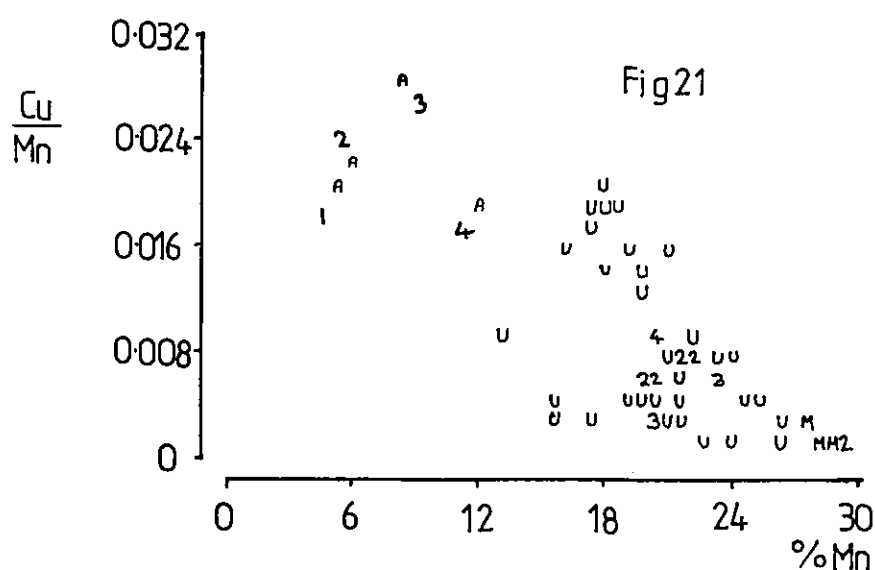
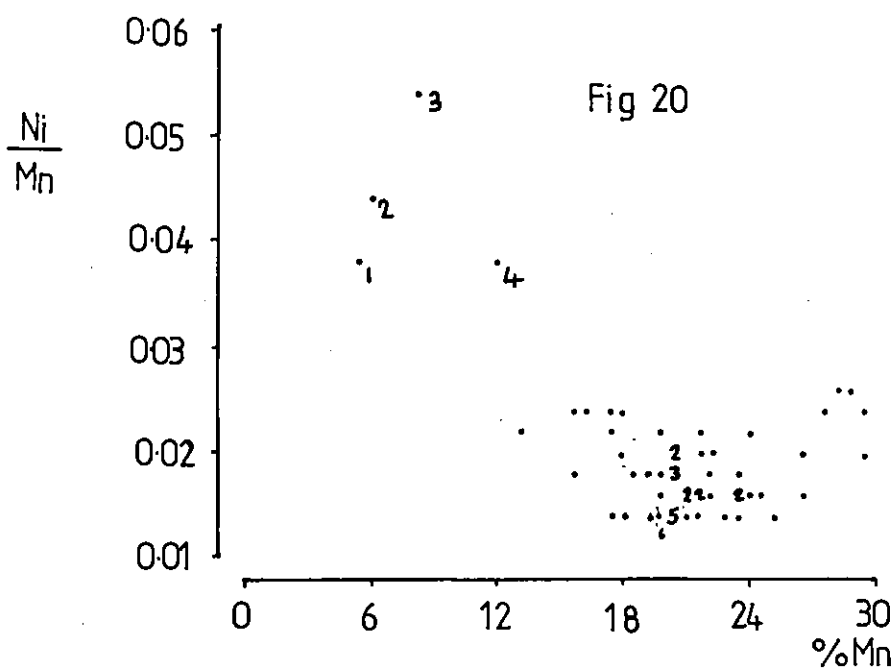
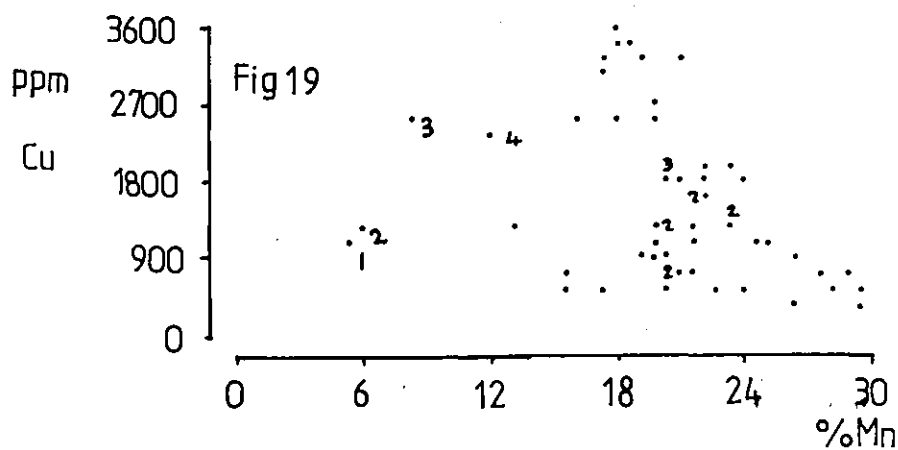


Fig. 19. Cu vs. Mn in the LI crusts. See Fig.3 for legend.

Figs. 20,21. Ni/Mn and Cu/Mn ratios vs. the Mn contents of the LI crusts. 1-4 represent samples from crust 053 1/1

(See section 3.3.2).

Trace metals associated dominantly with Mn are likely to be present in higher abundances in the 5 samples with high Mn contents and high Mn/Fe ratios. This is the case for Cd, Zn, Ni and Pb (Figs. 6-9). Conversely, elements associated more closely with Fe exhibit decreased abundances in high Mn/Fe crusts; these elements are Ba and Be (Figs. 10 + 12). Trace elements dominantly within the authigenic phase but with no particular affinity for Mn or Fe oxides show a positive relation with Mn and Fe only when the detrital contribution to the crust is important and the authigenic contribution is declining. Such elements are Ti, Sr, V and Ag (Figs. 13-18).

The inter-element associations are summarized below with weaker associations in parentheses:-

Al-K-Li-Na	- aluminosilicate
(Na-Mg)	- seasalt
Mn-Co-Mo (-Cd-Ni-Zn-Pb)	- SMnO_2
(Fe-Ba-Be-Cu-Al)	- $\text{FeOOH} \cdot \text{H}_2\text{O}$
Mn-Fe-V-Sr-Ag-Ti (-Pb)	- Mn and Fe oxides

The importance of mineralogical controls on crust chemistry is clearly observed on a plot of Ni/Mn : Mn (Fig. 20). Todorokite was found in all four samples of 053 1/1, which contained abundant phillipsite. These samples are marked 1-4 on Fig. 20. The high Ni content in nodule todorokite is well documented; the same is found in the crusts. Cu is also enriched in todorokite. In crust 053, however, Cu is less enriched relative to Mn than is Ni (Fig. 21), which may be a function of a low supply of Cu.

3.4 Trace element enrichment mechanisms of Mn and Fe oxides

Whilst positive correlations between Mn, Fe and trace metals in marine ferromanganese deposits suggest that the major oxide phases are important scavengers of trace metals from the water column, they reveal little about the mechanisms of incorporation. Data for the LI crusts suggest that they are accumulating directly from the water column, that there is a uniform mineralogical control on them

and that their chemistry is not influenced by diagenetic reactions. It may therefore be profitable to compare the crusts' chemistry with that which one may predict from the knowledge of the chemical properties of the pure oxide phases. Whilst several mechanisms have been proposed to explain trace element uptake by oxides (Table 8), only adsorption is considered in any detail here.

Table 8 Proposed trace element enrichment mechanisms
 of metal oxides

-
1. Adsorption
 - a. Coulombic (electrostatic)
 - b. Specific (chemical)
 - c. Hydroxide precipitation at the oxide -
 solution interface (James and Healy model).
 2. Formation of complex insoluble oxides (Hem 1977,
 Ruppert 1980).
 3. Formation of poorly soluble phosphate complexes on
 ferric oxides (Ruppert 1980).
 4. Co-precipitation involving redox reactions between
 Mn species and other metal ions (Hem 1978a, b).
-

3.4.1 Evidence for adsorption in the marine environment

Adsorption onto solid surfaces is a mechanism commonly invoked as a control on the distribution of chemical elements in seawater (Craig 1974, Brewer and Hao 1979) and as a mechanism to explain the trace-element enrichment of marine ferromanganese deposits (Goldberg 1954, Crerar and Barnes 1974, Glasby 1974). There is abundant circumstantial evidence that this is the case. Firstly, ocean waters are distinctly undersaturated in most elements with respect to their most insoluble phases (Murray and Brewer 1977). Since this cannot be attributed to lack of supply through geologic time, scavenging by

particulates has been invoked as an efficient removal process (Goldschmidt 1937, Krauskopf 1956, Turekian 1977).

Secondly, strong correlations between particulate Mn and certain trace elements have been observed in the Black Sea (Spencer et al. 1972, Pilipchuk and Volkov 1974) and in Saanich Inlet on Vancouver Island (Berrang and Grill 1974). Thirdly, significant correlations are noted between the Mn and Fe oxide phases and the trace element contents of ferromanganese deposits (e.g. Cronan 1980 and references therein).

Despite this evidence, there is a lack of understanding regarding both the mechanisms of adsorption and the degree to which they can explain observed trace element contents in both oxides and biogenic particulates. Whilst many laboratory studies have been made on the surface chemistry of both hydrous manganese dioxide (MnO_2) (e.g. Morgan and Stumm 1964, Murray et al. 1968, Posselt et al. 1968, McKenzie 1970, Loganathan and Bureau 1973, Murray 1974, 1975a, b, Balistrieri and Murray 1982 a) and iron oxide (e.g. Atkinson et al. 1968, Tewari et al. 1972, Kinniburgh et al. 1976, Balistrieri and Murray (1981, 1982b), it is difficult to extrapolate these with certainty to the marine environment. In particular, we cannot be certain that the pure solids investigated occur as discrete phases. Furthermore, it has been suggested (Neihof and Loeb 1972, Hunter and Liss 1979, 1982) that in natural seawater particles become coated in organic films which may alter their surface properties (Balistrieri et al. 1981).

3.4.2 Mechanisms of adsorption

The adsorption of metal ions by metal oxides may be considered in terms of both chemical and coulombic attractions (Grahame 1947, James and Healy 1972). The total change in the standard free energy of adsorption when a metal ion adsorbs onto a metal oxide surface, $\Delta G_{\text{ADS}}^{\circ}$

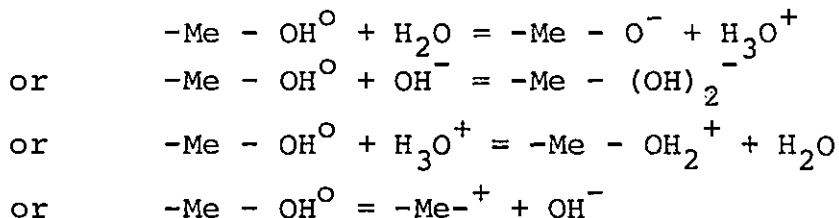
may be expressed as the sum of the change in electrochemical (coulombic) adsorption energy ($\Delta G^{\circ}_{\text{coul}}$), the change in total specific (chemical) adsorption energy ($\Delta G^{\circ}_{\text{chem}}$) and the change in secondary solvation energy ($\Delta G^{\circ}_{\text{solv}}$):-

$$\Delta G^{\circ}_{\text{ADS}} = \Delta G^{\circ}_{\text{coul}} + \Delta G^{\circ}_{\text{solv}} + \Delta G^{\circ}_{\text{chem}}$$

Each term will be examined in turn.

3.4.2.1 Electrostatic (electrochemical) adsorption

Solids in natural waters have electrically charged surfaces. The origin of the charge at the hydrated metal-oxide - solution interface may be viewed in terms of participation of the metal-hydroxide groups in acid-base reactions to produce a positively or negatively charged surface:-



In electrolyte solutions such as seawater, ions other than H^{+} are important in determining surface charge (Yates et al. 1974). The titratable charge of an oxide is the sum of the surface species which adsorb protons (e.g. $\text{Me} - \text{OH}_2^{+}$, $\text{Me} - \text{OH}_2 \text{ Cl}$) minus the sum of surface species which release protons during their formation (e.g. $\text{Me} - \text{O}^{-}$, $\text{Me} - \text{ONa}$). From this one may determine the pH of the point of zero charge (pH(PZC)) which is the pH value at which the solid surface is uncharged. Some values for the pH (PZC) of Mn and Fe oxides are given in Table 9.

Table 9 Comparison of the pH (PZC) for Mn and Fe oxides

Oxide	pH(PZC)	Reference
Hydrous Mn dioxide ¹	2.2	Murray (1974)
Hydrous Mn dioxide ²	1.5	Balistrieri and Murray (1982a)
SMnO_2	1.5	Healy et al. (1966)
Mn(II) manganite	1.8	Healy et al. (1966)
Amorphous Fe oxide	8.1	Kinniburgh (1973)
Amorphous Fe oxide	7.9	Davis and Leckie (1978)
Goethite ($\approx \text{FeOOH}$)	7.5	Balistrieri and Murray (1981)

¹ characterised by XRD peaks at 7.4, 2.43, 1.63Å⁰

² characterised by XRD peaks at 2.43, 1.43Å⁰

Table 9 indicates that hydrous MnO_2 should carry a negative surface charge at seawater pHs and would be expected to electrostatically adsorb cations at pHs greater than approximately 2. This has been observed by many workers (e.g. Morgan and Stumm 1964, Murray et al. 1968, Murray 1975a, Balistrieri and Murray 1982a). In addition, Murray (1975a) noted an increase in the amount of cation adsorbed with rising pH.

The situation is somewhat more uncertain for Fe oxides. Whilst Fe oxides have a pH dependent surface charge (Parks and De Bruyn 1962), the pH (PZC) of Fe oxide is close to the pH of seawater (Table 9) and varies according to its mode of formation and subsequent ageing. Its surface charge in seawater is uncertain. Goldberg (1965) and Goldberg + Arrhenius (1958) have stated that Fe oxides in seawater are positively charged. Goldberg (1954, 1965) has therefore proposed that Mn oxides adsorb cations from seawater and Fe oxides adsorb anions. Recent measurements of electrophoretic mobility, however, suggest that Fe oxides are negatively charged in seawater (Neihof and Loeb 1972). This has been attributed

to the adsorption of substances of both low and high (macro) molecular weight. Similar findings have been reported by Hunter and Liss (1979) for estuarine and coastal waters and by Tipping and Cooke (1982) for fresh-water iron oxides.

An idea of the possible importance of electrostatic adsorption as a trace element enrichment mechanism for marine Fe-Mn oxides may be obtained by comparing the actual cation content of the LI crusts with that predicted by theory.

To calculate the cation content of the ferromanganese minerals in the crusts the contribution of seasalt cations must first be removed. In the absence of chemical data on salt-free nodules, this must be calculated from first principles. The water content of ferromanganese nodules is approximately 45% of the bulk dry mass (Greenslate 1977). Since the salt content of seawater is 36%, the salt content of a nodule is $45 \times 0.036 = 1.6\%$ of the dry mass. From the mean composition of seawater, cations due to seasalt are then 4,500 ppm Na, 600 ppm Mg, 200 ppm Ca and 200 ppm K; subtracting from the bulk contents of the crusts yields cations within the ferromanganese oxides in the quantities 10,000 ppm Na, 3,000 ppm K, 9,000 ppm Mg, 24,000 ppm Ca, 5,500 ppm Co, 5,000 ppm Mn, 3,900 ppm Ni, 1,200 ppm Sr, 1,400 ppm Ba, 1,000 ppm Pb and 600 ppm Zn, a total of approximately 64,500 ppm cations. The calculation assumes that MnO_2 adsorbs Mn in similar quantities to Co (Murray 1975a) and that the contribution of other cations is negligible. The mean Mn content of the crusts is 20.4%, which gives a measured cation/Mn ratio of $64,500/204,000 = 0.32$.

Using alkalimetric titration curves, Murray (1974) has calculated surface charge values of approximately $100 \mu\text{C cm}^{-2}$ for synthetic MnO_2 at pH8 in 0.01 M NaCl, equivalent to $5 \times 10^{-6} \text{ Mm}^{-2}$ of divalent cations. Taking the surface area of synthetic MnO_2 to be $260 \text{ m}^2 \text{ g}^{-1}$ (Murray 1974), which is similar to that determined for 8MnO_2 -rich nodules (Buser and Grutter 1956, Halbach et al. 1975), this equals $1.3 \times 10^{-3} \text{ M cations g}^{-1} \text{ MnO}_2$,

or 0.07 M cations mole^{-1} Mn, which is the theoretical electrostatic adsorption capacity of MnO_2 . This compares with the measured cation/Mn ratio in the crusts of 0.32.

The theoretical ratio suggests that $0.07/0.32 = 22\%$ of the catio content of the crusts may be explained by electrostatic adsorption onto Mn oxides. This figure would be increased if electrostatic adsorption by Fe oxides was also taken into account.

3.4.2.2 Specific adsorption

There is abundant circumstantial and experimental evidence that mechanisms other than simple coulombic attraction are important to adsorption by metal oxides (see Murray and Brewer 1977 and references therein), a fact reflected by element selectivity sequences of the oxides. Experimentally determined selectivity sequences for MnO_2 and Fe oxides, plus the enrichment sequences of LI crusts over seawater are shown in Table 10.

Table 10 Trace element selectivity sequences of Mn oxide and Fe oxides, with the trace element enrichment sequence of LI crusts over seawater

1. Hydrrous MnO_2 (Murray 1975).

$\text{Co} > \text{Mn} > \text{Zn} > \text{Ni} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} > \text{K} = \text{Na}$

2. Amorphous Fe oxyhydroxide (Kinniburgh et al. 1976)

$\text{Pb} > (\text{Cu})^1 > \text{Zn} > \text{Ni} > \text{Cd} > \text{Co} > \text{Ba} > \text{Ca} > \text{Sr} > \text{Mg}$

3. Goethite (Grimme 1969)

$(\text{Cu}) > \text{Zn} > \text{Mn}$

4. LI crusts (this work)

$\text{Pb} > \text{Co} > \text{Ni} > \text{Cu} > \text{Zn} > \text{Ba} > \text{Cd} > \text{Sr} > \text{Ca} > \text{Mg}$

¹ Cu is shown in parentheses since at seawater pH, hydrolysis and precipitation reactions may affect its solubility

Table 10 shows the general similarity between laboratory determinations of metal oxide element selectivity sequences and the enrichment sequence of the LI crusts. Particularly noteworthy is the position of Co close to the head of the MnO_2 and LI crusts sequences, in comparison to its position in the middle of the Fe oxyhydroxide sequence. Both Co and Pb (which is at the head of the crusts' sequence) may be removed from seawater in their highest valency states (Co^{3+} , Pb^{4+} , Goldberg 1961). The necessary oxidation reaction can occur at the MnO_2 -seawater interface (Murray and Dillard 1979). The position of Pb and Co at the head of the LI crusts selectivity sequence suggests that the oxidation reaction effectively fixes the elements with the Mn oxide, whilst other elements remain free to partake in exchange reactions with ambient seawater.

Enrichment mechanisms other than electrostatic adsorption must also be invoked for Mo and V, which occur as oxyanions in seawater (MoO_4^{2-} , HVO_4^{2-} , Murray and Brewer 1977) and are associated with the crusts' Mn oxide phase. Ruppert (1980) has pointed out that the solubility of CaMoO_4 -like complexes are only 20 times that of the actual concentrations of the constituent ions in seawater and that such complexes may precipitate on Ca-bearing Mn oxides. The commonly observed association of Mo with Mn in widely differing marine environments (Berrang and Grill 1974, Pilipchuk and Volkov 1974, Moorby and Cronan in press, present work) does however, suggest a direct affinity of Mo for Mn.

The above discussion assumes that laboratory results may be extended to interpret field observations. In favour of this, Murray (1975b) has successfully used laboratory determined adsorption density for Co on synthetic hydrous MnO_2 to predict the Co content of suspended particulate Mn oxide in the Black Sea. Conversely, Ruppert (1980) used the same adsorption density to calculate the equilibrium concentrations of Co, Cu, Ni and Zn in synthetic 8MnO_2 in seawater. The values for Co, Cu and Ni are much lower than those in the crusts, whilst the Zn value is similar (Table 11).

Table 11 Concentrations of Co, Ni, Cu + Zn in synthetic
hydrous MnO₂ in equilibrium with seawater.
Calculated from the adsorption isotherm for
Co²⁺ ions (Murray 1975b)

	ppm			
	Co	Ni	Cu	Zn
Synthetic hydrous MnO ₂	25	480	100	540
LI crusts	5450	3860	1540	590

Table 12 Abundances and enrichments of elements in seawater
and the LI crusts

Element	Seawater concentration (mgKg ⁻¹)	Crust (ppm)	Crust/ seawater
Be ⁷	5.7 x 10 ⁻⁷	5	8.8 x 10 ⁶
Mg ⁷	1.3 x 10 ³	~ 10000	8
Ca ⁷	413	~ 25000	67
Sr ⁷	8	1190	149
Ba ⁷	4 x 10 ⁻²	1370	3.4 x 10 ⁴
Mn ⁷	2.7 x 10 ⁻⁵	204000	7.5 x 10 ⁹
Fe ⁵	4.2 x 10 ⁻⁵	170000	4.0 x 10 ⁹
Na ⁷	1.1 x 10 ⁴	2000	0.18
K ⁷	3.9 x 10 ²	6400	0.89
Li ⁷	0.18	5	17
Zn ¹	5.89 x 10 ⁻⁴	590	10 ⁶
Ni ¹	6.46 x 10 ⁻⁴	3860	6 x 10 ⁶
Cu ¹	3.18 x 10 ⁻⁴	1540	4.6 x 10 ⁶
Co ²	8 x 10 ⁻⁶	5450	6.8 x 10 ⁸
Ti ⁷	9.6 x 10 ⁻⁴	12000	1.2 x 10 ⁷
Cr ⁴	2.3 x 10 ⁻⁴	37	1.6 x 10 ⁵
Al ⁷	2 x 10 ⁻³	~ 4000	2 x 10 ⁶
Cd ¹	1.24 x 10 ⁻⁴	4	3.2 x 10 ⁴
Ag ⁷	4.3 x 10 ⁻⁵	5	1.2 x 10 ⁵
Pb ³	10 ⁻⁶	1020	10 ⁹
La ⁶	4.5 x 10 ⁻⁶	310	6.9 x 10 ⁷
Ce ⁶	2.8 x 10 ⁻⁶	970	3.5 x 10 ⁸
Nd ⁶	3.6 x 10 ⁻⁶	240	6.7 x 10 ⁷

Seawater data:-

¹ Bruland (1980)

² Robertson (1970)

³ Schaule & Patterson (1981)

⁴ Campbell & Yeats (1981)

⁵ Gordon et al. (1982)

⁶ Elderfield & Greaves (1982)

⁷ Murray & Brewer (1977)

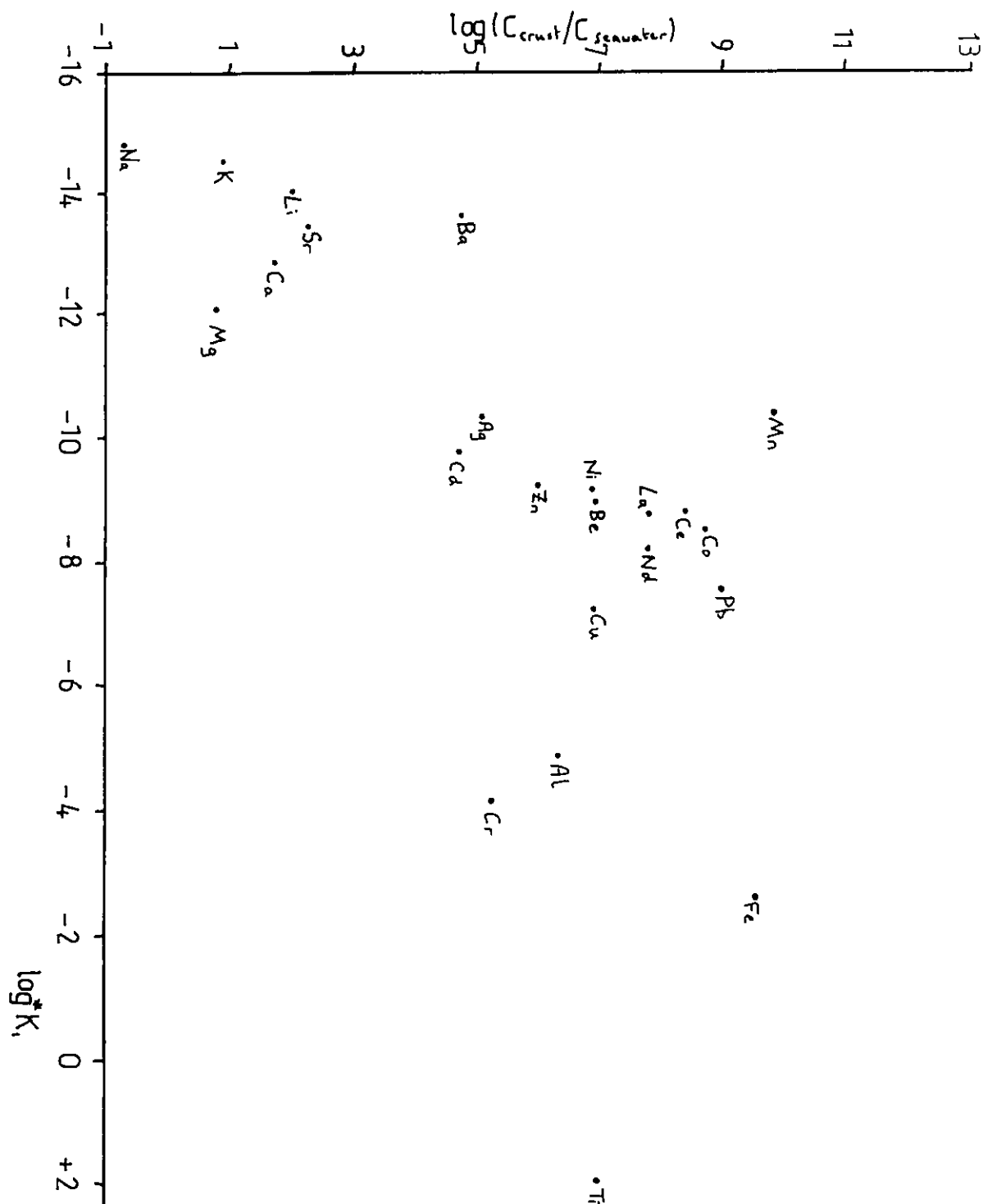


Fig.22 Plot of $\log(C_{\text{crust}}/C_{\text{seawater}})$ versus $\log^*K_1$ (the first hydrolysis constant of a metal).

Clearly it is premature to extend unequivocally laboratory results to the field. Current problems include the precise nature of colloidal oxides in natural seawater, the lack of laboratory experiments at seawater metal concentrations and the different time scales of laboratory experiments and natural systems. Concerning the third point, although laboratory experiments come to equilibrium within hours or days (Loganathan and Bureau 1973, Murray 1975a), we cannot be certain that this represents the equilibrium attained over a period similar to the residence

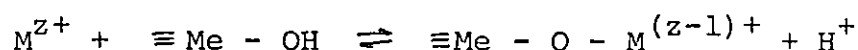
time for colloidal oxide flocs, which may be tens or hundreds of years. This may be particularly true for elements which can substitute for Mn(IV) in the MnO_2 lattice (e.g. Co.).

3.4.2.3 Models for specific adsorption

Despite the evidence for specific adsorption, the chemical processes involved therein are still poorly understood. However, three models have been suggested which can be viewed as working simultaneously - the stoichiometric reaction model, the James and Healy model, and ion substitution in the metal oxide structure.

3.4.2.3A The stoichiometric reaction model

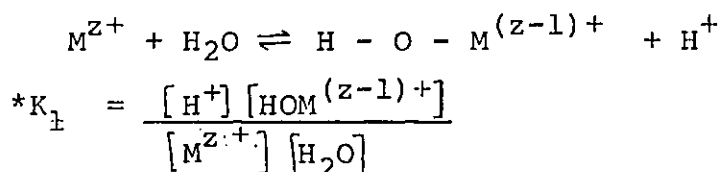
This model (Kurbatov et al. 1951, Stumm et al. 1970) is based on the observation that the specific adsorption of cations invariably involves proton exchange (Morgan and Stumm 1964, Stumm et al. 1970). According to the stoichiometric reaction model, the adsorption of a cation, M^{z+} , on the surface hydroxyl groups can be represented thus:-



$$\text{giving } *K_1^S (\text{app}) = \frac{[\text{H}^+] \{ \equiv \text{Me} - \text{O} - \text{M}^{(z-1)+} \}}{[\text{M}^{z+}] \{ \text{MeOH} \}}$$

where $*K_1^S (\text{app})$ = apparent equilibrium constant

Dugger et al (1964) showed that the Gibbs free energy or the bond strength of single metal-oxygen bonds on silica gel for various cations are linearly correlated to their $\log *K_1$ where $*K_1$ is the first hydrolysis constant for the reaction



In addition Schindler (1975) showed that $\log^* K_1^S$ (app) of silica gel for various cations are linearly correlated with $\log^* K_1$. This implies that the relative strength of metal-oxygen bonding is little affected by the host metal. If the stoichiometric reaction model is of importance, then the partitioning of cations between solid and liquid phases ($C_{\text{crust}}/C_{\text{sw}}$ = concentration in the crust/concentration in seawater, Table 12), should be positively correlated with the relative bond-strength between cation and metal represented by $*K_1^S$ (app) or with $*K_1$.

A plot of $\log^* K_1$ versus $\log C_{\text{crust}}/C_{\text{sw}}$ is shown in Figure 22. Values of $\log^* K_1$ are taken from Li (1981), values of C_{sw} are from Murray and Brewer (1977) except for Cr (Campbell + Yeats 1981), Cd, Zn, Ni and Cu (Bruland 1980), Pb (Schaule and Patterson (1978), Fe (Gordon et al. 1982) and the REE (Elderfield and Greaves 1982). Crust values are on a salt-free basis. A reasonable positive correlation is seen within the transition and REE groups. Since Mn precipitates from the water column rather than simply becoming enriched through adsorption, one would expect it to lie above the trend. Similarly one may explain the enrichment of Ba in terms of BaSO_4 precipitation. Overall, the alkaline earth metals show no positive correlation with $\log^* K$ and indeed Ba-Sr-Ca-Mg appear to be negatively correlated. Be, however, plots in an entirely different field to the other alkaline earth metals.

Furthermore, Ti, Al, Fe and Cu all fall below the regression line. The distinction between truly dissolved Fe and very fine colloidal Fe oxyhydroxide is difficult to make and the value given by Gordon et al. (1982) may therefore be an overestimate. Similar to Mn, one may intuitively expect it to lie above the general trend since it too precipitates from seawater. Li (1981) has suggested that the Ti concentration in seawater may also be overestimated. The low $C_{\text{crust}}/C_{\text{sw}}$ value for Cu may be explained by the formation of Cu-organic complexes. The affinity of Cu for organic material is well documented both from laboratory

work (Irvine and Williams 1953) and in the riverine environment (Sunda and Hanson 1979).

Neither V nor Mo are plotted on Figure 22. Both occur as oxyanions in seawater (HVO_4^{2-} , MoO_4^{2-}). Li (1981) has suggested that the strength of the bond between Fe at the Fe oxide surface and O of the oxyanion is inversely related to both the first and second dissociation contents of the acid H_2AO_x , not to $\log^* K_1$. On the other hand, Cr is plotted and falls well below the general trend. Whilst its speciation in seawater is uncertain, Elderfield (1970) has suggested that the most probable species are $[(\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4)]^+$ and $(\text{CrO}_4)^{2-}$. The latter is thermodynamically favoured and Cranston and Murray (1978) have found Cr (VI) to be the dominant species in a Pacific Ocean profile.

In summary, whilst the general positive correlation between $\log C_{\text{crust}}/C_{\text{sw}}$ and $\log^* K_1$ suggests that the stoichiometric reaction model is tenable for many elements, there are sufficient anomalies to necessitate the examination of other trace element enrichment mechanisms for ferromanganese oxide.

3.4.2.3B James + Healy Model

A second model to explain adsorption data was developed by James and Healy (1972) to rationalise the evidence that cation adsorption is closely related to hydrolysis and precipitation (Grimme 1969). The model is based on the observation that for most metal oxides adsorption is small at low pHs but increases rapidly over a small pH change which is much lower than that at which precipitation or hydrolysis would be expected in the bulk solution. The model suggests that the high electric field at the surface has the effect of reducing the solubility product of the metal hydroxide and rendering it less soluble at the solid-solution boundary.

The interaction of cations with hydrous MnO_2 is more complex than either the stoichiometric reaction model or the James and Healy model in isolation. Alkalimetric titrations during cation adsorption experiments (Murray et al. 1968, Murray 1975a, Balistrieri and Murray (1982) indicate that proton exchange is important. The observation of Murray (1975b) that the amount of Co adsorbed by hydrous MnO_2 increased sharply at pH6, much lower than that required for Co (II) hydrolysis or precipitation, lends support to the James and Healy model.

3.4.2.3C Structure of the metal oxide

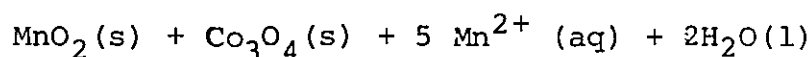
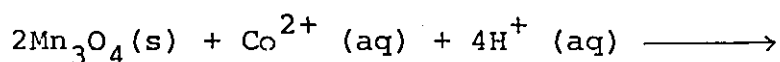
A third factor in determining specific adsorption may be the structure of the metal oxide. This is illustrated by the strong enrichment of Co in δMnO_2 , which has been explained by the oxidation of Co(II) to Co(III) in seawater (Goldberg 1961, Burns 1976). The oxidation of Co on the surface of hydrous MnO_2 has been verified experimentally by Murray and Dillard (1979) using X-ray photoelectron spectroscopy, and Dillard et al. (1982) have used the same technique to show the presence of Co (III) in ferromanganese nodules. Burns (1976) has suggested that Co^{3+} substitution for Mn^{4+} is likely in the MnO_6 octahedra, since it has a similar ionic radius ($0.54\text{\AA}$), and may explain its enrichment in δMnO_2 .

3.4.3 Other trace element enrichment mechanisms in Mn and Fe oxides

Both Hem (1977) and Ruppert (1980) have pointed out that the ferrites of Ni, Cu and Zn are highly insoluble; indeed these three elements are supersaturated in seawater relative to their ferrites. Only Cu shows any relation to Fe in the crusts, whilst Ni and Zn are moderately correlated with Mn. The strong correlation of Ni, Zn + Cu with Mn in Fe-Mn nodules led Ruppert (1980) to suggest that these three elements, plus Co, may form complex oxides with Mn such as MeMnO_3 , MeMn_2O_4 + MeMn_3O_8 . Such compounds could be revealed by the electron probe as isolated, very

high Cu/Ni/Zn/Co enrichments. Although Ruppert (1980) has found Cu and Ni values up to 30% in small areas of nodules, the bulk of probe work (e.g. Burns and Fuerstenau 1966, Cronan and Tooms 1968, Burns and Burns 1978, Moore et al. 1981) has not revealed such concentrations and tends to show fairly constant Cu/Ni to Mn ratios. In addition, some of the Mn in such compounds would be in the trivalent state, which has not been observed in Fe-Mn nodules (Burns and Burns 1977, Dillard et al. 1982). Alternatively, however, one can argue that if the structures have dimensions less than the diameter of the probe's electron beam (2 μm), such high Cu/Ni/Co/Zn contents will not be observed. Furthermore, the structures may be metastable and undergo diagenetic changes soon after initial deposition.

Hem (1978a, b) has proposed a reaction that couples the oxidation of Co, Ni and Pb to the disproportionation of hausmannite (Mn_3O_4) resulting in a pronounced decrease in the equilibrium solubility of those elements. The reaction is of the form:-

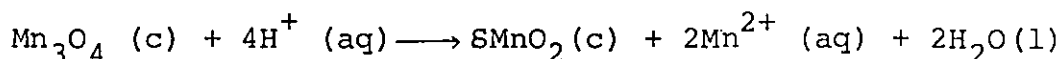


The concentrations predicted by Hem's reaction are similar to those found in seawater. For $(\text{Mn}^{2+}) = 10^{-9} \text{ Ml}^{-1}$:-

	Ml^{-1}	
	<u>Predicted Conc.</u>	<u>Actual Conc.</u>
Pb^{2+}	$10^{-10.7}$	$10^{-11.3}$
Co^{2+}	$10^{-10.5}$	$10^{-9.8}$
Ni^{2+}	10^{-8}	$10^{-8.1}$

Murray and Dillard (1979) have criticised the reaction mechanism for Co on two grounds; firstly that Mn (III) is unlikely to occur in nodules in significant amounts (Burns 1970, see also Dillard et al. 1982) and secondly that insufficient Co^{2+} could be brought together to form

the coherent spinel structure. The first objection may be overcome if the proposed reaction occurs on oxide flocs in the water column. Bricker (1965) has studied the oxidation products of Mn^{2+} in aqueous systems at 25°C . He found that the initial product of oxidation when solution pH was raised in the presence of air was hausmannite, Mn_3O_4 . Stumm and Giovanoli (1976) have observed similar results in simulated lake water. Bricker obtained 8MnO_2 by acidification of suspensions of Mn_3O_4 in the presence of oxygen:-



It is the coupling of this reaction with the oxidation of $\text{Ni}^{2+}/\text{Pb}^{2+}/\text{Co}^{2+}$ which Hem (1978a, b) is proposing. Unfortunately, little is known about the oxidation state of particulate Mn in seawater. Klinkhammer and Bender (1980) have suggested that the dissolved Mn distribution in the water column may be a function of seawater equilibrium with a metastable oxide similar to hausmannite. If this is the case then the Hem reaction may be envisaged, at least for Co + Pb. Since Ni has not been observed in the trivalent state in marine Fe-Mn deposits, one cannot invoke the Hem reaction for it.

Ruppert (1980) has suggested that poorly soluble phosphate complexes forming at the surface of Fe oxides may cause Pb + Sr enrichment in nodules. However, the lack of Fe-Sr-Pb-P correlations mitigates against this.

3.4.4 Summary of proposed trace element enrichment mechanisms

Whilst one cannot rule out any enrichment mechanism with the present data set, deductions as to the likelihood of each may be made. The low pH(ZPC) of Mn oxide suggests a probable role for electrostatic adsorption. However, simplistic calculations indicate that electrostatic interaction can only account for 25% of the crusts' cation complement. Clearly specific processes are important, although their precise nature is unclear.

The stoichiometric reaction model can, however, partially explain the observed partitioning of metals between seawater and Fe-Mn oxides. For some elements, notably the transition elements Co, Mo, V, Ni, Zn and also Pb + Sr, specific attractions are important, although the precise nature of these are difficult to ascertain. Substitution of similar-sized cations for Mn^{4+} in the 8MnO_2 lattice may be an important stabilization mechanism for certain adsorbed elements.

It is impossible to make an accurate judgement concerning the possibility of the formation of single element spinels or complex oxides. Certainly it would be profitable to study further the relative importance of the enrichment mechanisms.

3.5 Crust O62 1/3

Crust O62 1/3 (Plate 5) exhibits some unusual characteristics. Firstly, it is 70 mm thick, which apart from O62 3/3 from the same dredge haul is twice the thickness of any other crust and four times the mean thickness. Secondly it is the only crust to show goethite by XRD, and thirdly it exhibits a very different chemistry to the other crusts.

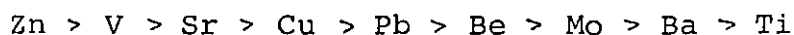
Structurally, the crust consists of 5 layers separated by rather indistinct lines of weakness. Six samples (A-F) were taken:- A and B from the upper and lower parts respectively of the topmost layer; samples C, D, E and F from progressively lower layers. No substrate was attached, although O62 3/3 is associated with a francolite substrate.

Mineralogically, A and B consist of 8MnO_2 and amorphous $\text{FeOOH}\cdot\text{H}_2\text{O}$, which is typical of the crusts. Goethite was definitely identified by XRD in samples C and D (Fig. 2), and small amounts may occur in E and F. For a specific mineral to be identified by XRD in a mineralic mixture, it typically occurs in at least 5% abundance. The broadness of the goethite peak suggests

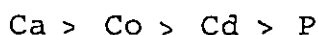
it is poorly crystalline and probably therefore needs to occur in greater than 5% abundance for XRD identification.

Goethite has been identified previously in nodules (Burns and Burns 1977). Moorby (1978) has found goethite in some Atlantic nodules and suggests that goethite-containing nodules have low Mn/Fe ratios, often much less than unity. Whilst the Mn/Fe ratios of the goethitic samples are lower than average for crusts in the same depth range (Fig. 23), they are nevertheless around unity and show no clear relation to the apparent goethite contents. It is interesting to note that goethite is found in the thickest crust and is known to be an ageing product of $\text{FeOOH} \cdot x\text{H}_2\text{O}$ (e.g. Murray 1979). However, its greater abundance in layers C and D over E and F mitigates against its occurrence purely as an ageing phenomenon. One possibility is that Mn and Fe need to be segregated effectively before the goethite lattice may develop. This would explain the generally low Mn/Fe ratios of goethite-containing nodules (e.g. Moorby 1978), but cannot explain the presence of goethite in the present samples.

A comparison of the mean element abundances in 062 1/3 with the mean of eleven other crusts in the 2500-3500 m depth range is shown in Table 13. The mean abundances of Be, Ti, Sr, Ba, Cu, Pb, Zn, Mo and V in 062 1/3 are more than one standard deviation above the mean of other crusts from the same depth range, whilst Ca, P, Co and Cd are depleted below the same level. The enrichment sequence is:-



whilst the depletion sequence is:-



062 3/3, dredged nearby, is also enriched in Cu and Ba, but is depleted in Mo (Table 8). All other elements are within 20% of the mean of 2500-3500 m crusts.

Plots of element content versus depth in the crust reveal different enrichment patterns for each element (Fig. 23). Except for P (depleted) and Sr (enriched),

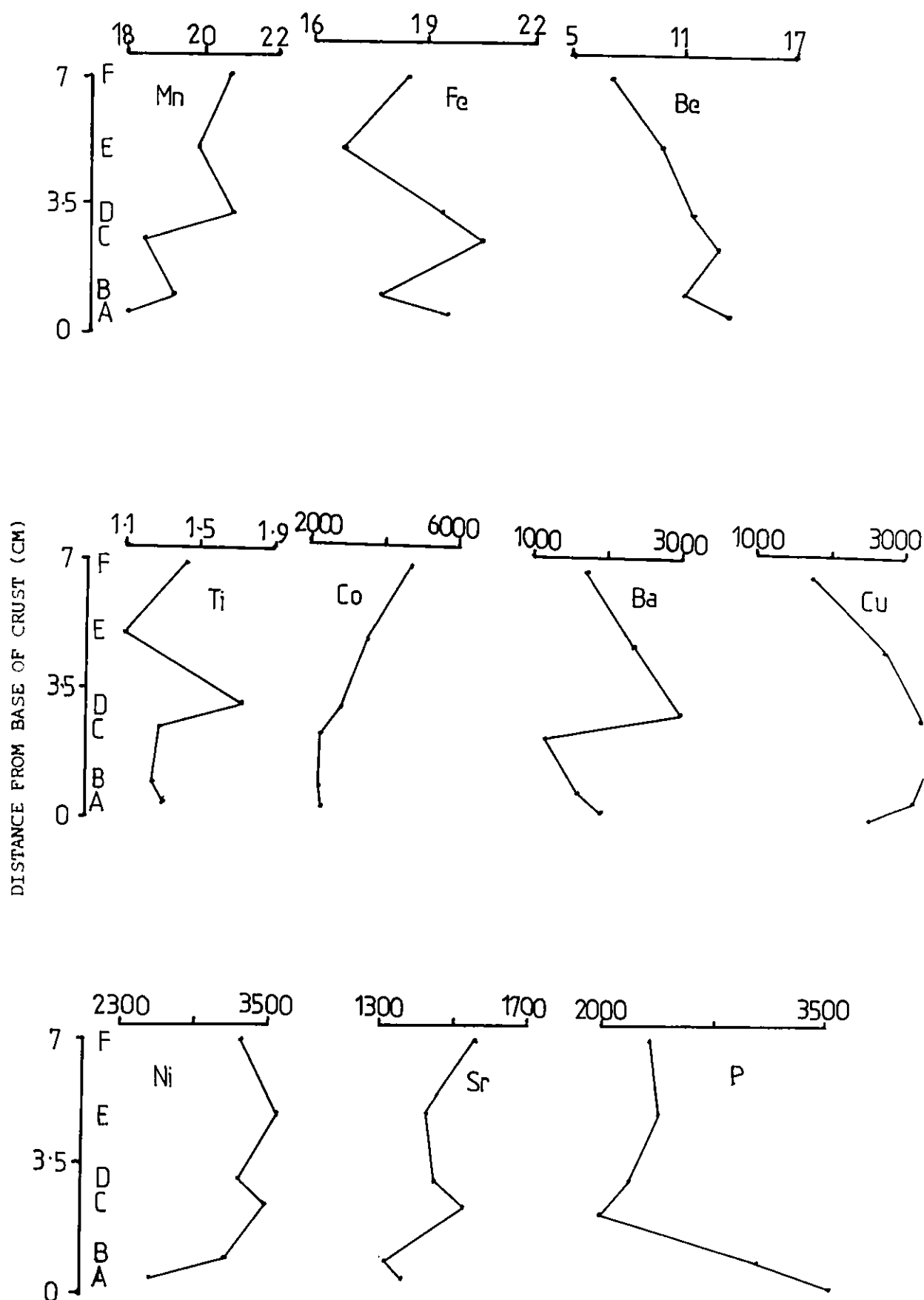


Fig. 23. Vertical distribution of elements through crust 062 1/3.

A-F represent sample identifications. Mn, Fe, Ti, in weight %.

Other elements in ppm.

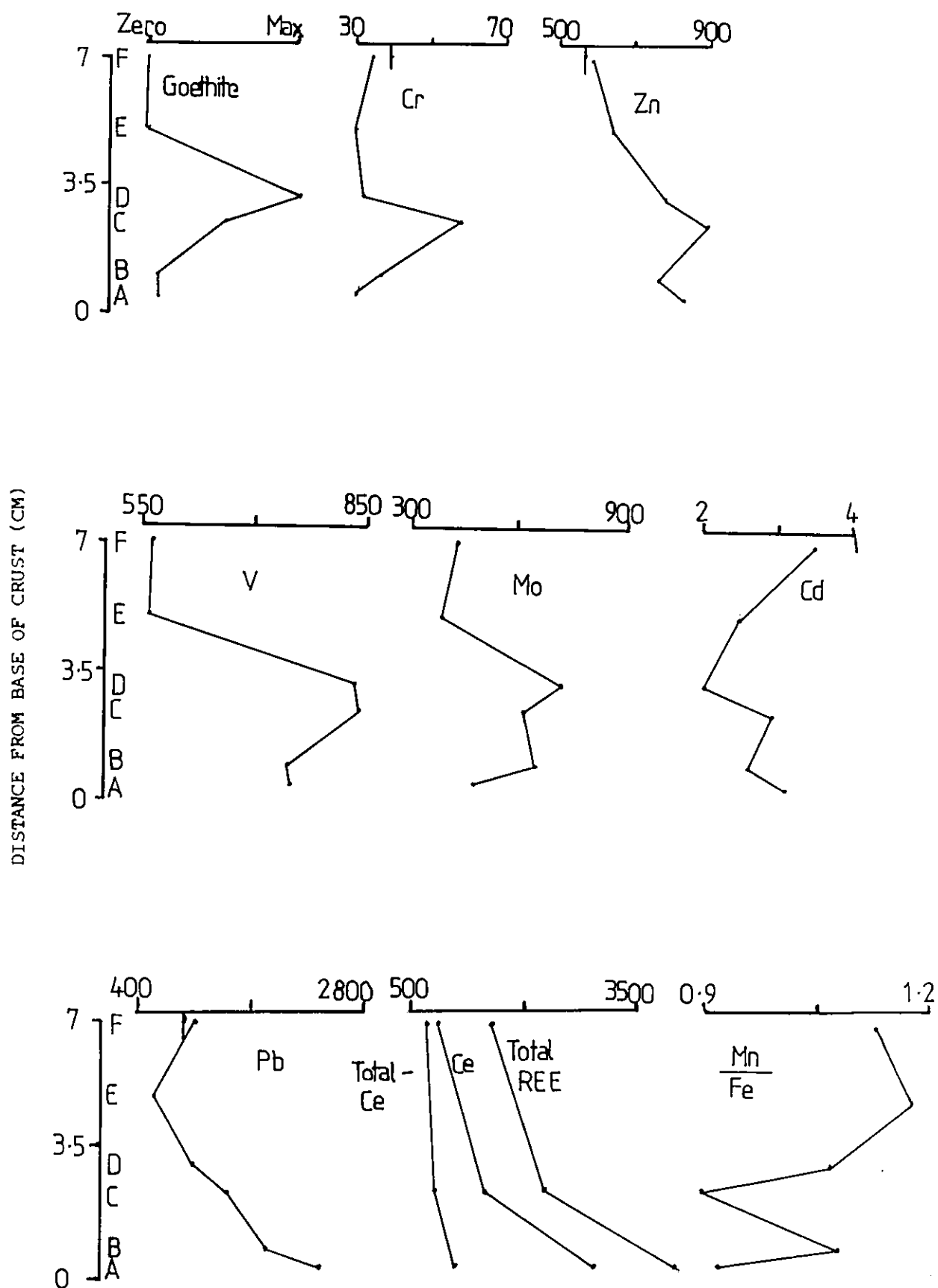


Fig. 23. (cont.)

Table 13 Mean element abundances of O62 1/3, O62 3/3 and other crusts from 2500-3500m, with the standard deviations of element abundances in the 2500-3500 m crusts and Z scores of O62 1/3 and O62 3/3 with respect to the 2500-3500 m crusts.

Element	Mean	S.D.	Mean		Z ¹	
	2500-3500		O62 1/3	O62 3/3	O62 1/3	O62 3/3
Mn	21.7	2.55	19.5	18.9	-0.9	-1.1
Fe	19.1	2.19	19.2	17.8	0.05	-0.6
Ca	2.48	0.23	2.04	2.46	-2.1	-0.09
Be	5.14	0.97	11.20	5.39	2.25	0.3
Cr	38.8	11.50	36.6	32.5	-0.2	-0.5
Mg	1.07	0.15	0.93	0.96	-0.9	-0.7
P	3550	884	2610	3250	1.1	-0.3
Ti	11300	1708	13700	13000	1.4	1.0
Co	5530	1738	2940	4850	-1.5	-0.4
Sr	1250	76	1470	1140	2.9	-1.4
Ba	1320	384	1900	1710	1.5	1.0
Cu	1370	546	2340	2410	2.7	1.9
Ni	3650	779	3150	3430	-0.6	-0.3
Pb	880	264	1500	900	2.3	0.08
Zn	570	31	770	550	6.5	-0.6
Mo	440	78	580	320	1.8	-1.5
V	570	33	750	460	5.5	-3.3
Ag	5.61	1.65	5.12	4.43	-0.3	-0.7
Cd	4.04	0.87	2.88	3.33	-1.3	-0.8

Mn, Fe, Ca, Mg in weight %

Other elements in ppm

$$l_z = \frac{X - \bar{X}_{2500-3500}}{(\text{standard deviation})_{2500-3500}}$$

most elements occur in average abundances in sample A. Environmental conditions during recent periods of accretion would therefore seem to be no different to elsewhere in the same depth regime. Other enriched elements show two basic patterns:- firstly, elements for which abundances appear related to the abundance of goethite - V, Mo, Zn + Cu - and secondly, elements which occur in decreasing abundance up the crust - Be, Pb and Ce. Zn and Cu show affinity to both groups whilst Ti, Ba and Sr do not fit into either.

It would be premature to suggest a mineralogical control of V, Mo, Zn and Cu by goethite. It is possible that conditions favouring the occurrence of goethite also favours the enrichment of these elements. This is of particular interest in the case of Mo, which in all other crusts is closely associated with Mn (see Fig. 4).

It is interesting to note that Ce is fractionated from the 3+ REE in O62 1/3. The greater than average total REE contents of samples D and F are due almost entirely to the higher abundances of Ce, whilst the 3 + REE contents are almost constant throughout the crusts (Fig. 23). In comparison, the distribution of Pb is similar to that of Ce, whilst that of Co is reversed. All these elements are removed from seawater in their higher valence state (Section 4.6.5). Co is closely associated with Mn. In addition, Cd, which is also associated with Mn, is depleted in O62 1/3, whilst Ce, Cu, Ba and Be, all associated with Fe, are enriched. It appears that Fe exerts a greater control on the trace element geochemistry of O62 1/3 than in most crusts.

Overall, however, there is no unifying explanation to account for the trace element geochemistry of O62 1/3. Enriched/depleted elements show no obvious chemical characteristics. At present, therefore, its unusual chemistry must remain unexplained.

3.6 Summary

This study has confirmed the strong Mn-Co-Ni association found in previously described seamount encrustations and nodules. In addition, it has elucidated a strong Mn-Mo association and has revealed subtler trace element partitioning between SMnO_2 and $\text{FeOOH} \cdot x\text{H}_2\text{O}$ in the hydrogenous end-member of the ferromanganese spectrum. Specifically, Cd, Ni, Zn and Pb are associated more closely with SMnO_2 whilst Ba, Cu and Be are more closely associated with $\text{FeOOH} \cdot x\text{H}_2\text{O}$. Ti, V, Sr + Ag show no obvious partitioning.

Crust 062 1/3 has a remarkable trace element complement which cannot be explained by the partitioning described above.

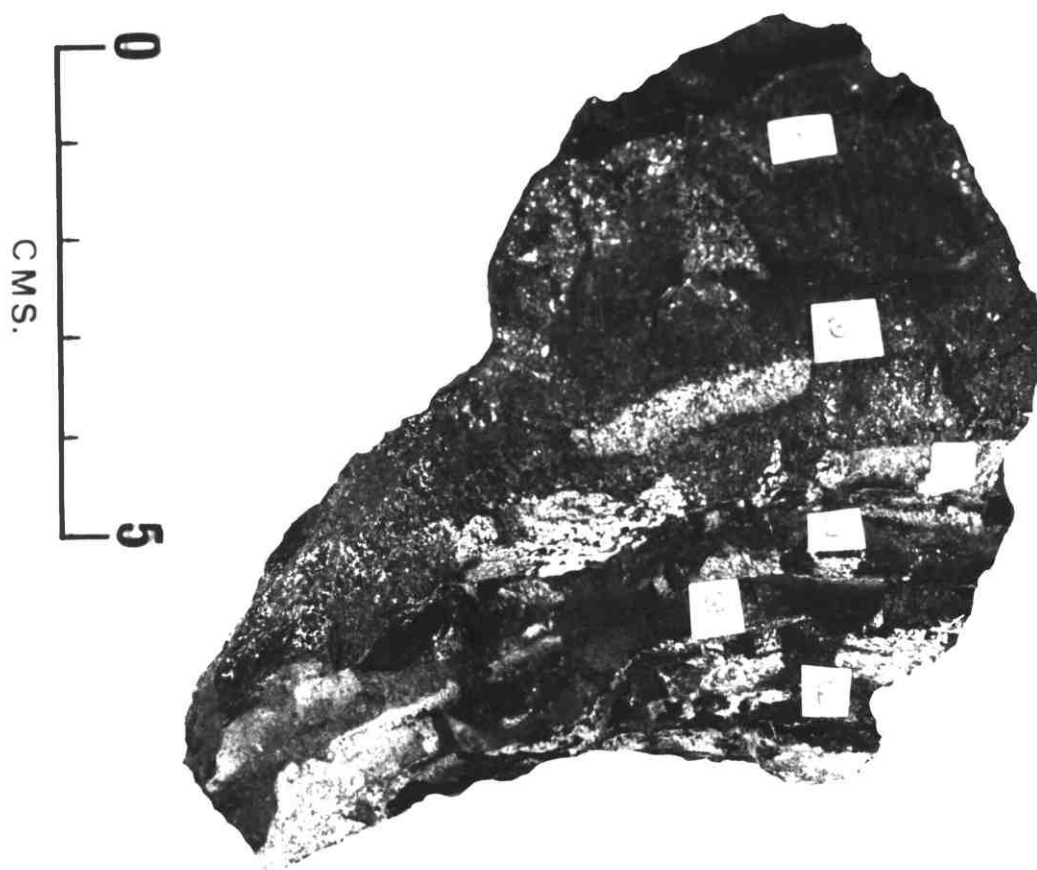


Plate 5 Sample 062 1/3

CHAPTER 4 CHEMICAL VARIABILITY

4.1 Introduction

Important chemical variability in Mn nodules and encrustations has been found on all scales, from inter-oceans to within individual nodules.

Regional variations in the composition of abyssal Pacific nodules have been discussed by Price and Calvert (1970), Calvert and Price (1977), Piper and Williamson (1977) and Greenslate et al. (1979). Piper and Williamson have suggested that nodules with high Mn/Fe ratios and high (Ni + Cu) contents tend to occur in areas where primary productivity is high and the sediment-accumulation rates low. One such area is the NE equatorial Pacific, the so-called 'ore-grade' belt of nodules, and similar findings have been made by Calvert and Price (1977) using factor analysis. Superimposed on such large scale regional variations, local environment changes can also produce variations in nodule composition. Cronan and Tooms (1967) found quite large compositional differences between two morphologically distinct populations in a small area on the flanks of Carlsberg Ridge. Similar compositional variations were observed between morphologically similar nodules collected in different topographical settings in the same area. Calvert et al. (1978) have described variations in the Mn/Fe ratio and minor element content of a suite of nodules from a small area of the NE equatorial Pacific. They explain the variation in terms of different degrees of diagenesis in the associated sediment related to the rate of sedimentation, which in turn is related to the topography of the region. In general, although subtle chemical variations occur in regions of low topographic relief (Friedrich and Plüger 1974), greater variability is seen in areas of highly dissected topography.

Significant variations in chemical composition also occur within individual nodules (Cronan and Tooms 1967, Raab 1972, Piper and Williamson 1981). Raab (1972) has found variations of up to 100% in trace metal content within individual nodules, and similar variations have been determined between different layers of single nodules using

electron probe analysis (Burns and Fuerstenau 1966, Moore et al. 1981). Piper and Williamson (1981) have interpreted the variability between individual layers in terms of the relative element contributions from seawater and interstitial water sources.

4.2 Intra-crust variability

The observed variability within nodules suggests that a similar analysis may be worthwhile for the crust samples examined in this study. Thus in cases where crusts were thick enough, more than one sample was taken, and where distinct layers were observed, samples were taken from each layer (see Section 2.3).

A principal component analysis on the LI crusts using the 10 elements Mn, Fe, Cu, Ni, Co, Pb, Zn, Ca, Al + Ti shows that the most important factor controlling overall chemical variability in the crusts is their non-oxide content (Table 14).

Table 14 Rotated factor loadings from principal component analysis of the 59 LI crusts using 10 element data

	Factor 1	Factor 2	Factor 3	Factor 4
Mn	-0.57	0.72	-0.19	0.09
Fe	-0.89	0.25	0.04	0.04
Ca	0.06	0.15	-0.09	0.95
Al	0.82	-0.38	0.27	-0.15
Ti	-0.81	0.09	0.03	-0.19
Co	-0.25	0.80	-0.49	-0.00
Cu	0.12	-0.19	0.93	-0.10
Ni	0.21	0.92	0.02	0.22
Pb	-0.66	0.47	-0.17	-0.26
Zn	-0.52	0.57	0.53	0.02
% variance accounted for	33	28	15	10

The same factors seem to control intra-crust variability. Comparison of sub-samples which have similar Al (+ Ca) contents show that their compositions are very similar (Fig. 24). For most elements sub-samples are within 10% of each other, whilst analytical precision is around 5% (Appendix 3).

Rising Al contents yield lower (Mn + Fe) contents. Additionally, because aluminosilicate substrates have Mn/Fe ratios of approximately 0.1 (Table 2), incorporation of substrate material into the crust, either through replacement by oxides or through sampling procedures, leads to a decrease in the Mn/Fe ratio. For example, sample O50 4/6A, from the upper part of that crust, has an Al content of 0.76%, a Mn content of 25.0% and an Fe content of 19.8%, giving a Mn/Fe ratio of 1.26. O50 4/6B, from the lower section of the crust, has an Al content of 1.92%, Mn = 20.6% and Fe = 18.52%, giving Mn/Fe = 1.11. Leaching studies (this work, Moore et al. 1981) suggest that as much as half the Al in a ferromanganese deposit of low Al content may be present in the oxide phases. This may amount to 0.4% Al w/w in the LI crusts. Thus O50 4/6B contains $1.9 - 0.4 = 1.5\%$ Al in the detrital phases. Assuming the detrital material has the same composition as the substrate (Table 2), $1.5 \times 11/7.92\%$ Fe is present in the detrital phase - i.e. 2.1%. The non-detrital Fe content of the crust is thus $18.52 - 2.1 = 16.42\%$, giving a Mn/Fe ratio of 1.25. Similar calculations yield a non-detrital Mn/Fe ratio of 1.32 for O50 4/6A, similar to the non-detrital Mn/Fe ratio of O50 4/6B.

Compared to nodules therefore, LI encrustations show very little intra-crust variability other than for aluminosilicate associated elements. One may explain this in terms of the single source of metals in crusts, their uniform mineralogy, and the dual source in nodules.

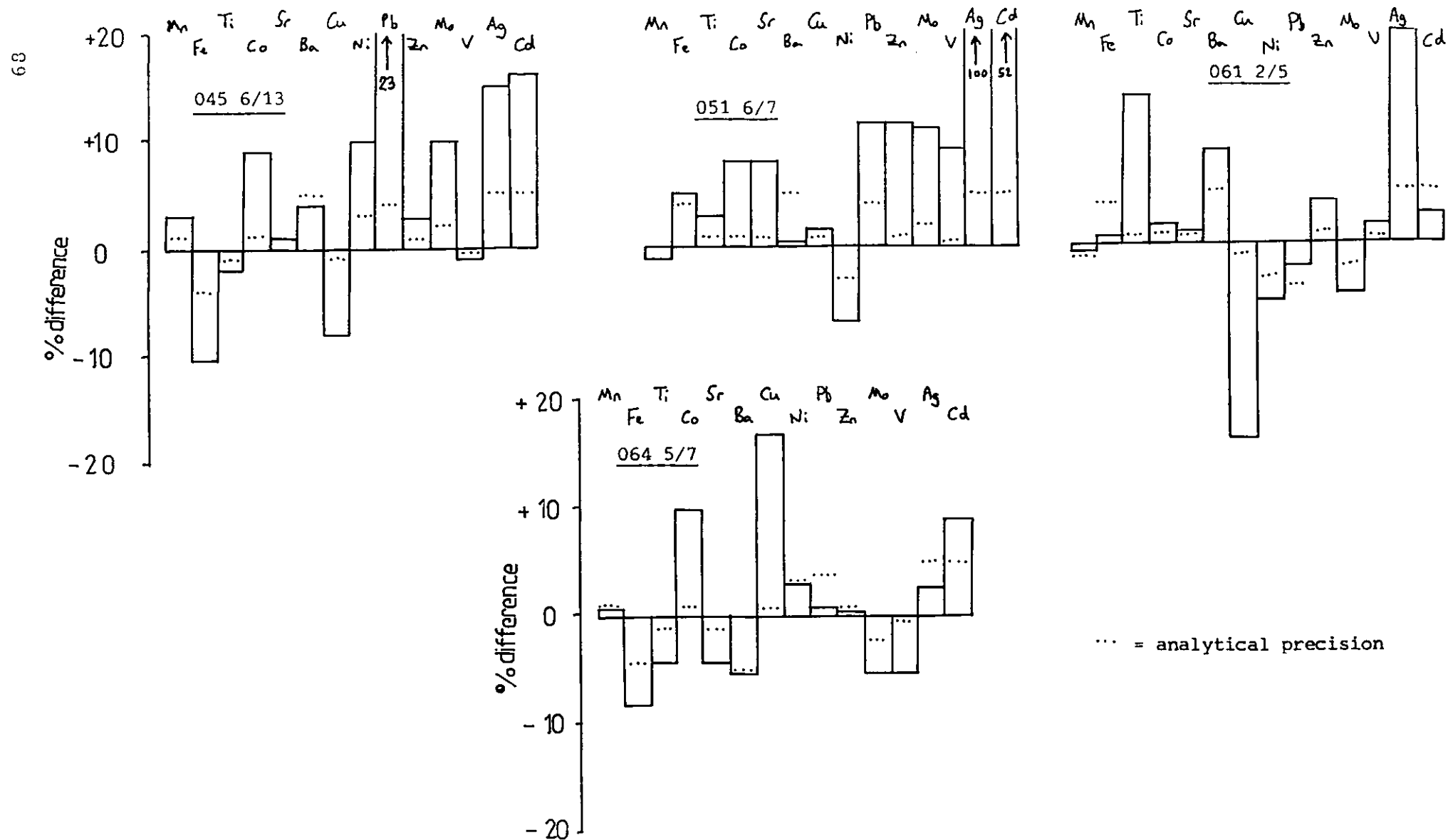


Fig. 24. Compositional differences between sub-samples from the same crust.

4.3 Within-station variability

Insufficient samples were obtained at any one station to perform an analysis of variance. Visual inspection of the data suggests that within-station variability is generally of similar magnitude to within-crust variability and is controlled by variations in the aluminosilicate content of the crusts.

One exception is the two crusts from station 058, at 1,200 m depth, which show large compositional differences (Appendix 4). This suggests that local environmental factors may affect crust composition, at least within the 1-2 km depth range.

4.4 Variability throughout the sample suite

Analysis of variance is a technique which enables us to accept or reject a null hypothesis that 2 or more groups of samples are derived from the same population, at a preset confidence level. In the present case we are concerned with the variability in the chemical compositions of the LI crust samples.

The technique divides population variance into between-group variance and within-group variance. The former is a measure of the difference between group means, and the latter reflects the dispersion of values within each group. The ratio of these values is denoted the F-ratio. The larger the F-ratio, the more confident we are that the groups are derived from populations with different means.

Since the Line Islands material is well controlled with respect to its environmental setting, an analysis of variance procedure will aid us to examine the effect of various environmental parameters on crust chemistry. The data set, which excluded francolite and aluminosilicate contaminated crusts, was divided into the following groups and sub-groups according to variations in:-

1. Associated substrates

- i) basalt with the original mineralogy intact; no weathering products
- ii) phillipsite and clay $\equiv$ weathered basaltic material
- iii) francolite (see section 2.1 on substrate descriptions).

2. Latitude

- i) more than 5°N
- ii) more than 5°S

Insufficient samples were procured from 5°S - 5°N to form a sub-group.

3. Depth

- i) 1000 - 2000 m
- ii) 2000 - 2500 m
- iii) 2500 - 3500 m
- iv) > 3500 m

Depth ranges were chosen with oceanographical factors in mind and in an attempt to keep sample numbers similar in each group. 2000 m represents the approximate boundary of intermediate and deep water; 2500 m the boundary of Pacific Deep Water and Pacific Bottom Water (Chapter 8).

Throughout the analysis of variance procedure the 95% confidence interval was used.

4.4.1 Independence of variables

Unequivocal interpretation of an analysis of variance requires that the variables are mutually independent. This is not the case in the present work, which is hampered by small data sets. Non-independence occurs in the following ways:-

- 1. Depth - substrate. 4 of the 7 'intact basalt' samples are from depths < 2,000 m; the mean depths of each substrate are given in Table 15.

Table 15 Mean depths of samples divided according to substrate type

	Mean depth	Standard deviation	No. of samples
'intact' basalt	1850	870	7
phillipsite/clay	3150	1100	27
francolite	2500	200	14

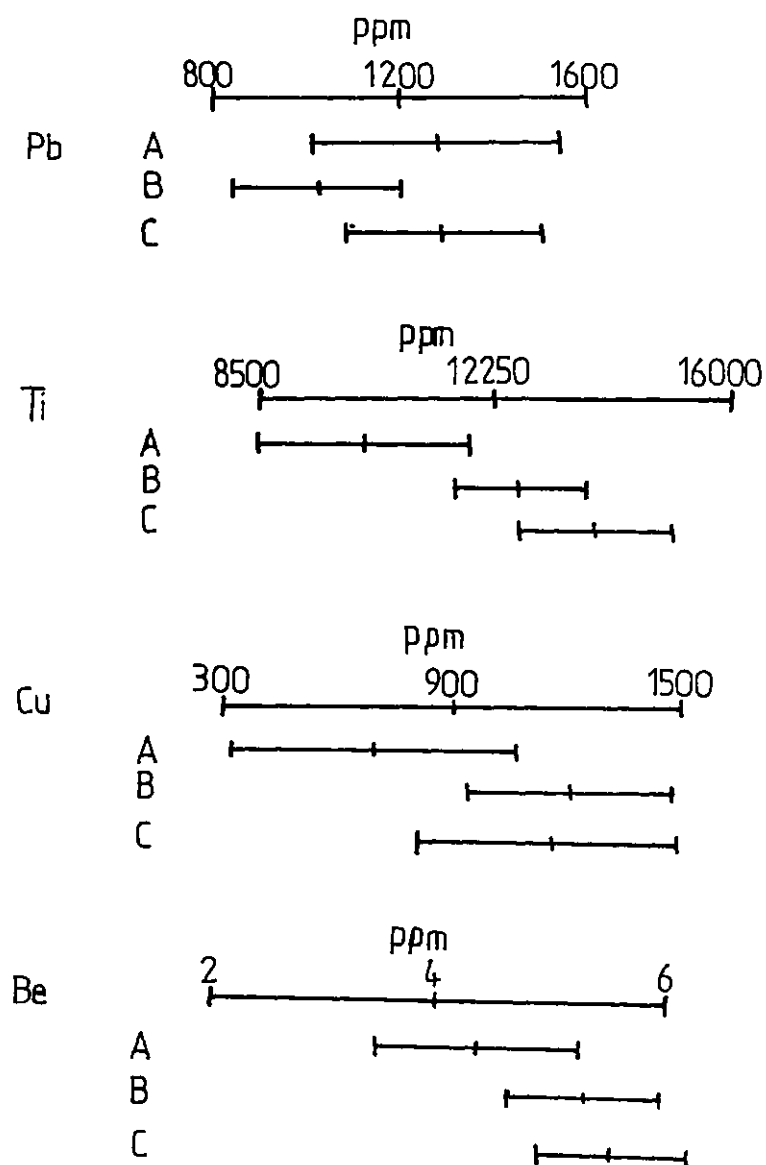


Fig. 25. 95% confidence intervals for Pb, Ti, Cu and Be derived from the analysis of variance procedure on the LI crusts, with respect to substrate type.
 A= 'intact basalt'
 B= phillipsite/smectite
 C= francolite

Table 17 Analysis of Variance with respect to latitudeNumber of samples $> 5^{\circ}\text{N} = 30$ Number of samples $> 5^{\circ}\text{S} = 8$

Element t	Mn -1.28	Fe 1.07	Cu 1.29	Ni -1.67	Ti 3.64	Be 4.04	Cr -1.23	Sr 1.73
Degrees freedom	36	36	36	7	36	35	36	36
Signif- icance	0.21	0.29	0.21	0.14	<u>0.0009</u>	<u>0.0003</u>	0.23	0.09

Element t	Pb 2.17	Zn 0.09	V 0.91	Ba 3.40	$\frac{\text{Mn}}{\text{Fe}}$ -1.55	Co -0.75	Mo -0.06
Degrees freedom	36	36	36	36	36	36	36
Signif- icance	<u>0.04</u>	0.93	0.37	<u>0.002</u>	0.13	0.46	0.95

Positive t values indicate the population with the greater mean is $> 5^{\circ}\text{N}$

- - significant at 0.05

= - significant at 0.01

Table 18 Analysis of Variance with respect to depth

4 subsets :-<2000 m, 2000 m -2500 m, 2500 m - 3500 m, > 3500 m

Degrees of freedom :- 3/36

Fcrit 0.05 = 2.86

Fcrit 0.01 = 4.38

Element F	Mn 11.42	Fe 4.52	Be 3.10	Cr 1.31	Ti 5.41	Sr 1.34	Cu 6.52
Element F	Ni 14.68	Pb 3.02	Zn 4.61	Mo 4.71	V 2.05	Ba 2.60	Ag 1.51
Element F	Co 17.28	Cd 17.61					

Table 19 Analysis of Variance with respect to depth.
Comparison of samples from >2000 m with samples
from >2000 m

Element	Mn	Fe	Ti	Zn	Cr	Be	Ba
t	5.84	-3.77	-1.02	2.44	-0.24	-4.06	-2.65
Df	38	38	38	38	38	23	38
Signif- icance	0.0000	0.0006	0.31	0.02	0.81	0.0005	0.01

Element	Sr	Cu	Pb	Ca	Ni	Mo	Cd
t	-1.46	-5.84	3.84	4.27	3.72	3.54	4.61
Df	29	34	17	5	5	38	5
Signif- icance	0.16	0.0000	0.001	0.008	0.01	0.001	0.006

Negative values indicate the > 2000 m population has the greater mean.

Examination of the depth - substrate relationship in Table 15 and the element-depth relationships indicates that the elemental variations noted here with respect to substrate could all be interpreted instead in terms of depth. The relatively high concentrations in 'intact' basalt crusts of elements occurring in high amounts in shoaler crusts (Co, Cd, Ni, Mo) supports this possibility. For Ti, the predominance of francolite substrates north of 5°N. also allows the interpretation of variation due to regional trends.

4.4.3 Analysis of variance with respect to latitude

The t values and levels of significance listed in Table 17 suggest that regional trends may occur for Be, Ti, Ba and Pb, which appear to occur in higher concentrations north of 5°N. Whilst it is interesting to note that Craig et al. (1982) have also reported a weak regional trend for Ti, the small data set presented here and the lack of independence amongst the variables precludes the possibility of a definitive statement concerning possible regional trends.

4.4.4 Analysis of variance with respect to depth

The results of the analysis of variance on the four depth subsets 1000-2000 m, 2000 - 2500 m, 2500 - 3500 m, >3500 m are given in Table 18. Depth plots for each element giving means and standard deviations are shown in Fig. 26. Many elements show great variation with depth, particularly Mn, and elements strongly or moderately associated with Mn (Ni, Zn, Mo, Co, Cd). Iron and elements moderately associated with Fe (Ba, Be, Cu), and Ti + Pb, which do not correlate well with either Mn or Fe individually, also show depth variations.

Further statistical tests were performed on elements exhibiting significant depth variability. Table 19 suggests that much variability exists between crusts from <2000m and crusts from >2000 m. Student t tests were performed on these 2 groups (Table 19). Mn, Pb and the Mn-associated elements Zn, Co, Ni, Mo + Cd occur in significantly higher concentrations in crusts from <2000 m, whilst Fe, Be, Ba + Cu are present in greater amounts below 2 000 m. Ti, Cr + Sr show no significant differences between these data sets.

Table 20 shows the results of an analysis of variance for the three subsets 2000 - 2500 m, 2500 - 3500 m + >3500 m. Elements included in the analysis are those which exhibited significant variation in the initial analysis of variance. Ti, Co, Cu + Zn give $F > F_{critical}$. Fig. 26 shows that for Ti + Co this is due to higher values in the depth range 2000 - 2500 m. For Cu + Zn, higher values within the 2500 - 3500 m depth range are explicable by their anomalously high concentrations in crust 062 1/3 (see Section 3.5). This is borne out by the results in Tables 21 + 22. The former indicates that no significant differences exist for Cu, Zn + V between the sub-groups at depths >2000 m if goethite-containing samples are removed, whilst the latter gives a measure of the subgroup differences if goethite-containing samples are removed or retained. A discussion of the chemistry of crust 062 1/3, which contains goethite, is given in section 3.5.

Table 20 Analysis of Variance with respect to depth

Excluding samples < 2000m

Subsets: 2000 m - 2500 m, 2500 - 3500 m, > 3500 m.

Degrees of freedom :- 2/31

$F_{\text{critical } 0.05} = 3.30$

$F_{\text{critical } 0.01} = 5.34$

Element	Mn	Fe	Ti	Pb	Cu	Zn	Ba	Co	Ni	Mo	Cd
F	0.58	0.05	7.55	1.71	4.47	3.45	0.47	4.84	1.14	0.90	0.51

Table 21 Analysis of Variance with respect to depth

Excluding samples < 2000m

Excluding samples containing goethite (from 062 1/3)

Subsets: 2000 - 2500 m, 2500 - 3500 m, > 3500 m

Element	Cu	Zn	V
F	1.06	3.25	0.45

$F_{\text{critical } 0.05} = 3.37$

Table 22 Analysis of Variance with respect to depth

F test on subsets 2500 - 3500 m, 2000 - 2500 plus > 3500 m.

Element	Cu	Zn	
significance	0.01	0.03	including goethite containing samples
significance	0.20	0.59	excluding " " "

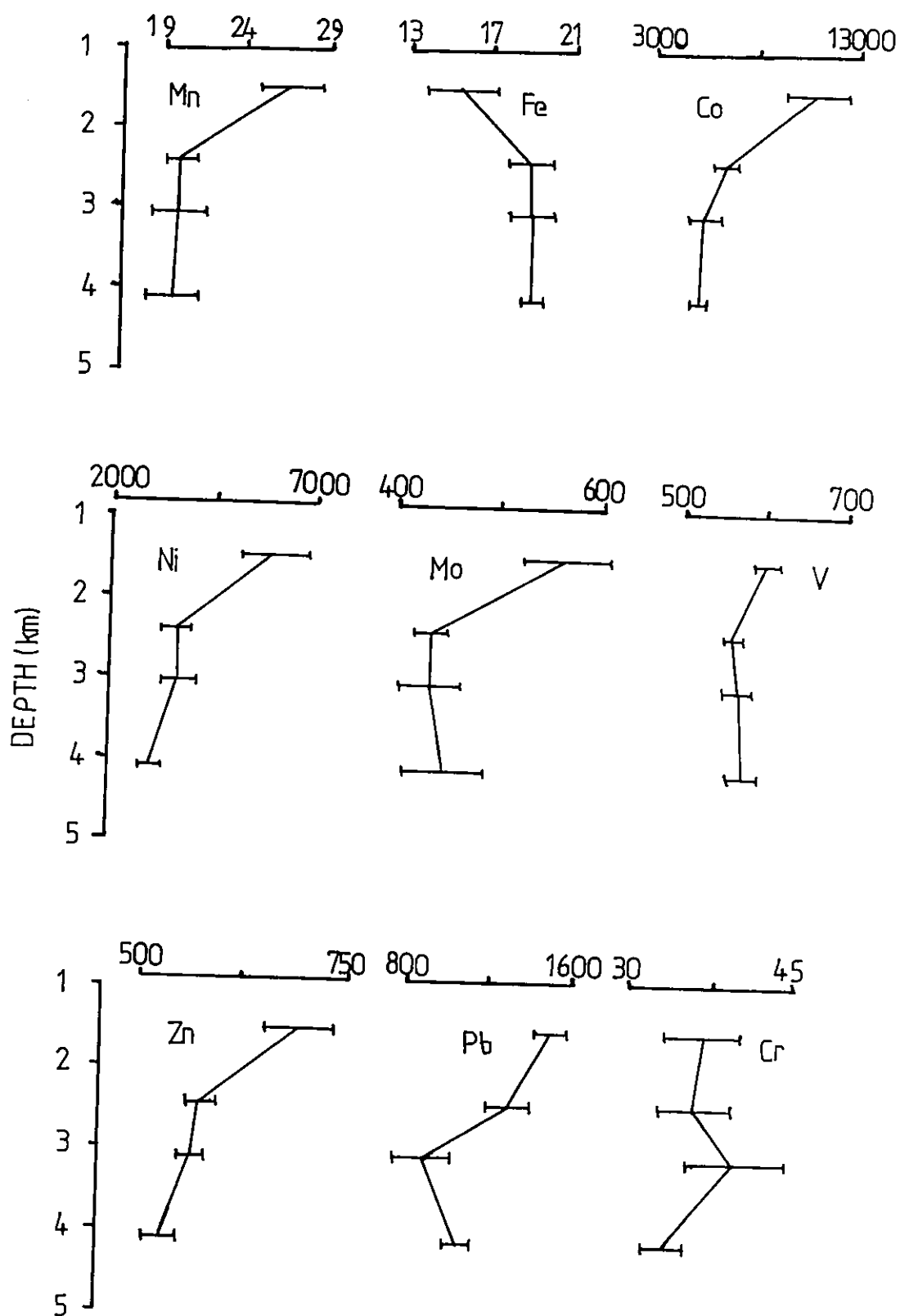


Fig. 26. Variation with water depth of element abundances in the LI crusts. Horizontal bars represent one standard deviation. Mn, Fe, in weight%. Other elements in ppm.

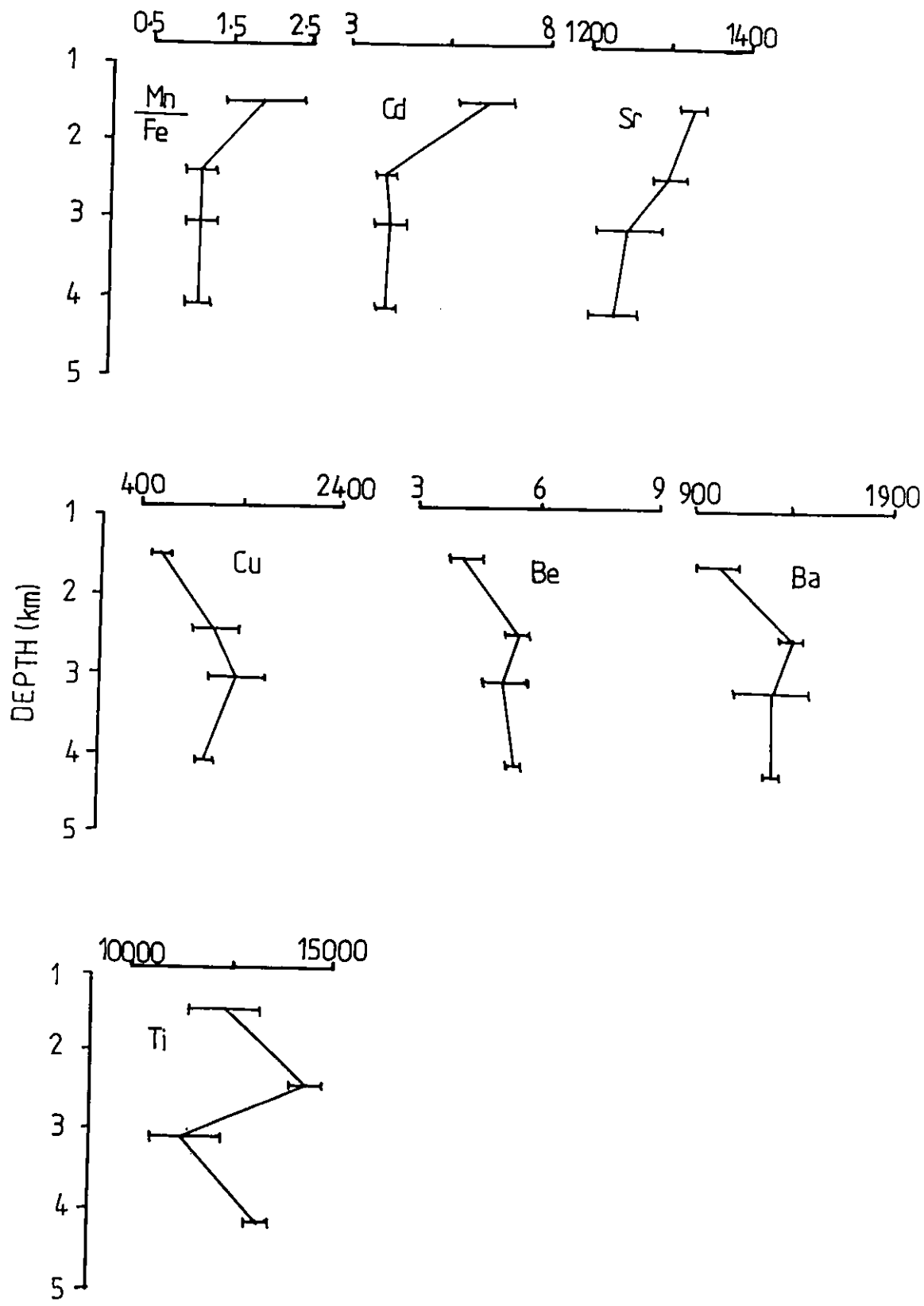


Fig. 26. (cont.)

The results of the statistical tests described above are summarized in Table 23. It can be seen that for Mn, Fe + many trace elements two sample populations exist. Mn, Mn-associated elements Ni, Zn, Co, Cd + Mo, + Pb, which has some association with Mn (Fig. 9), occur in higher amounts between 1 + 2 km, whilst Fe and the Fe-associated elements Ba, Be + Cu occur in higher amounts below 2 km. Only one population is discernable for Cr, Sr, V + Ag. From Fig. 26 it can be seen that the Mn/Fe ratio is higher between 1 + 2 km, and is very constant below that depth. Co exhibits a decreasing trend down to 2500 m, whilst Ti, alone, occurs in significantly higher concentrations between 2 + 2½ km. In this case, substrate and regional variations may also be invoked to explain the distribution (Sections 4.4.1 + 4.4.2).

The standard deviation bars in Fig. 26 indicate that the spread of Mn, Fe, Co, Cd, Ni, Mo, Zn and Mn/Fe values is greater above 2000 m than below. Pb + Cu show the opposite trend, whilst V, Be, Ag, Cr, Ti, Ba + Sr show no obvious trend with depth.

Finally, it is particularly noteworthy that apart from Co + Ti no significant variations were found in the distribution of any element at any depth below 2000 m. The same is true of Co + Ti below 2500 m.

4.5 Subsidence of ocean crust

Sclater et al. (1971) have shown that for much of the ocean floor younger than 80 My there is a simple relation between depth and age which can be explained by a simple cooling model. Parsons and Sclater (1977) have further suggested that the relationship holds for within-plate volcanic edifices such as the Line Islands Archipelago. To invoke a depth-related process as a control on the chemistry of ferromanganese crusts we must be certain that the crusts accumulated at the dredging depth throughout their history. Conversely, if the crusts have accumulated over a wide depth range, is this reflected in their chemistry?

Table 23 Summary of analysis of variance procedure with respect to depth. Element populations with significantly different means (95% level).

<u>Element</u> Depth Range	Mn	Ni	Pb	Zn	Co	Cd	Mo	Ti
1000-2000	X	X	X	X	XX	X	X	
2000-2500					X			X
2500-3500								
> 3500								
> 2000								

<u>Element</u> Depth Range	Fe	Be	Cr	Sr	V	Ba	Ag	Cu
1000-2000								
2000-2500								
2500-3500								
> 3500								
> 2000	X	X				X		

X = population with greater mean

XX = population with greatest mean, where more than one population is significantly greater than the rest.

We may examine this problem by 'backtracking' along the ocean crust subsidence curve of Sclater et al. (1971) (Fig. 27). Dividing the thickness of a crust by its growth rate gives the time since onset of development. Backtracking for that timespan Δt from a starting point given by the age of the substrate yields a depth change ΔH (Fig. 27). Important assumptions must be made in this procedure - the age of the substrate, the growth rate of the crusts, and that the crusts commenced development soon after the substrate formed.

K-Ar dates for late-stage volcanism in the LI cluster around 75-85 My (see section 1.2) whilst the youngest date determined is 40 My. Two ages for the onset of development of crusts have therefore been assumed, 40 My and 80 My.

Whilst nodules exhibit a wide range of growth rates, from 0-150 mm 10^{-6} y (Ku 1977, Reyss et al. 1982), and whilst individual nodules may have variable growth rates through time (Heye 1975), it appears that nodules without a

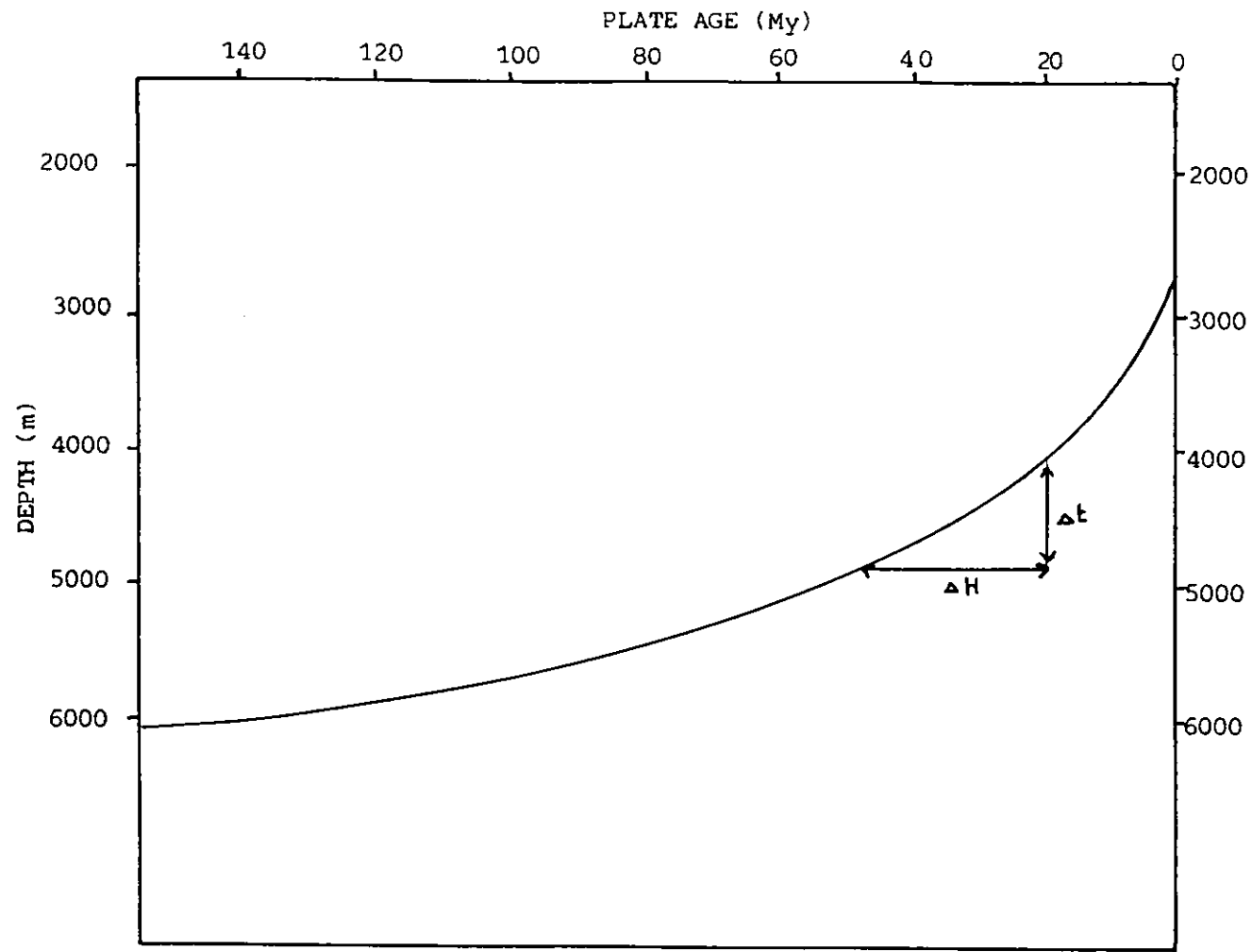


Fig.27 Subsidence path of oceanic basement. After Parsons and Sclater (1977).

diagenetic influence typically accumulate at the rate of 1-5 mm My⁻¹ (see Ku 1977, Ku et al. 1982). Again, two growth rates have been assumed in the calculations - 1 mm My⁻¹ and 5 mm My⁻¹.

The parameters which maximise the calculated subsidence are 1 mm My⁻¹ and an age of 40 My. Table 24 shows that for most crusts depth has not increased by more than 500 m during their growth history and that in most cases the depth of accumulation probably differed by less than 100 m. Furthermore, because most crusts have substrates of francolite or highly weathered volcanic breccias, their onset of development will have been well after late-stage volcanism in the region. Indeed, even if the crusts have accumulated at the slow rate of 0.5 mm My⁻¹, one would expect to find more crusts thicker than say 30 mm.

The very thickest crusts (70 mm) would have developed within a wide range if one assumes a low growth rate. There is, however, no chemical evidence to support this; nor, however, is there any evidence to support a rapid growth rate.

Table 24 Subsidence of ocean crust during development of ferromanganese crusts, using assumed age of substrate and growth rate

Crust thickness (mm)	1(min.)	15(Mode)	70 (Max.)	
Growth rate (mm My ⁻¹)	Age(My)	Subsidence (m)		
5	80	0	0	200
5	40	0	50	400
1	80	0	200	1900
1	40	0	450	1500 ¹

¹crust thickness of 35 mm used. 70 mm would elevate ocean crust above sea level at onset of development

Since significant changes in the chemistry of crusts appear to occur at around 2 km depth, crusts dredged just below this level may be expected to be the most sensitive indicators of subsidence. (Dredges 055, 063, 064). The similar chemistry of the whole group and throughout individual crusts mitigates against significant depth changes.

In conclusion, it is very likely that the suite of crusts studied here accumulated at or very close to the depth at which they were dredged.

Chemical variability with respect to depth may therefore be examined using the known depth of dredging.

4.6 Discussion

4.6.1 General Considerations

Although a larger data set would obviate the problem concerning the independence of variables, it is nevertheless clear from the analysis of variance procedure and correlation analysis that a depth-related process affecting the Mn/Fe ratio is the main factor controlling chemical variability within the crusts. Since there is no discernable variability with substrate types, halmyrolysis as a direct source of metals may be ruled out, although it may contribute indirectly by supplying metals to the water column. Furthermore, the rust colour of the aluminosilicate substrates suggests that much of the Fe is present as Fe oxide. The low Mn/Fe ratio of the substrates suggests that the Fe is not derived from seawater in the same way as the crusts and is most probably weathered from the original rock. Comparison of the Fe/Al ratio of fresh basalt (0.98, Krauskopf 1967) with those of phillipsite-smectite substrates (~ 1.3 , Table 2) indicates the apparent immobility of Fe in the weathering process and precludes halmyrolysis as a major source of Fe to the crusts. Only in cases where replacement of the substrate has occurred may the nature of the substrate be important to the chemical

composition of the crusts and their variability.

The low within-crust variability, the lack of a relationship between chemistry and crust thickness and the identical mineralogy and apparent crystallinity of crusts of all thickness rules out the possibility of significant diagenesis within the crusts. A process of accumulation of trace-metal-enriched Fe-Mn oxide flocs directly from the water column is invoked to explain the chemistry and development of the crusts, perhaps coupled with further metal enrichment at or very close to the crust-water interface.

4.6.2 Relation to dissolved species

Recent work (Bruland 1980 and references therein) has shown that the distribution of many trace elements in the water column is controlled by their involvement in the biogeochemical cycle. These include Cd, Zn, Ni, Cu (Fig. 28), Sr + Ba. Fixation within both the organic tissue and skeletons of organisms results in trace metal depletion of the photic zone, whilst oxidative decay and/or dissolution of those phases releases the metals at greater depth. Fig. 28 shows that the greatest diversity of Cd, Zn and Ni, at least, occurs within the upper kilometre of the water column, whilst crust chemistry exhibits the greatest variability above and below approximately two kilometres. For these elements, the concentration in seawater cannot be a limiting control on the concentration in crusts; their correlation with Mn (Tables 6 & 7) suggests that an affinity to Mn oxide and the variation in Mn/Fe ratio with depth may be more important factors.

The situation for Cu is different in that the higher seawater concentrations at depth are reflected in the crusts (Figs. 28 + 26). The strong affinity of Cu for organic material (Irvine and Williams 1953, Sunda and Hanson 1979) suggests that Cu may form organic complexes, thus inhibiting adsorption onto oxide flocs. Breakdown

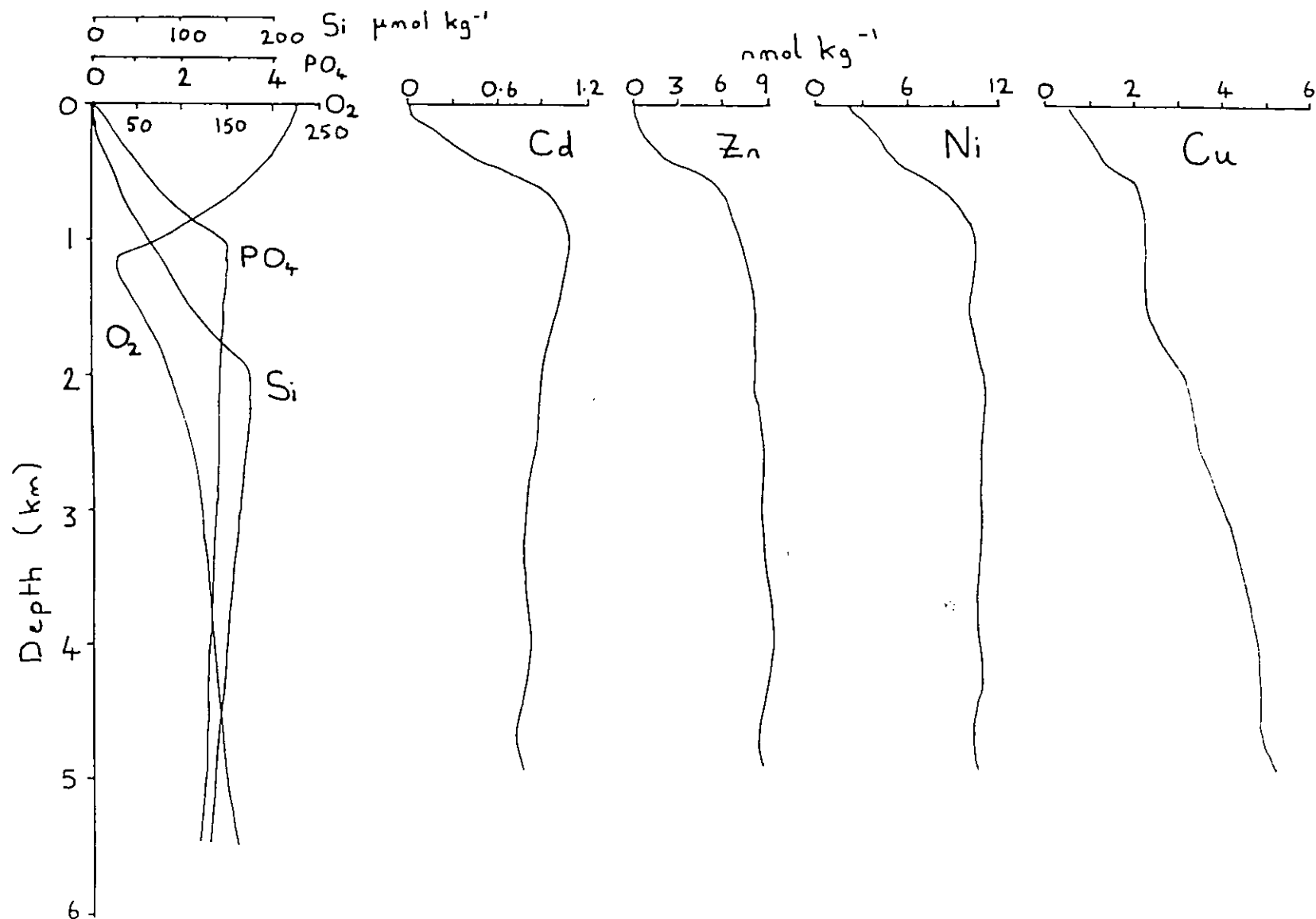


FIG. 28. Dissolved metal, phosphate, oxygen and Si profiles from a North Pacific station (33°N 145°W). From Bruland (1980)

of these complexes in deep water or at the sediment-water interface (Klinkhammer 1980) may lead to enhanced adsorption in deeper water. This concept is supported by a plot of $\log$ (crust concentration/seawater concentration) versus the $\log$ of the first hydrolysis constant of the metal ion (Fig. 22) on which Cu plots below the general trend for the transition elements.

4.6.3 Mn/Fe ratios

From the analysis within the previous sections, it is concluded that it is the surface properties and crystal chemistry of the Mn oxide + Fe oxide floccs which are the dominant controls on the trace element chemistry of the crusts. Possible causes of variation in the Mn/Fe ratios are therefore of major importance.

Cronan (1980) has shown that on average nodules with similar mineralogy from different oceans have contrasting chemical compositions (Table 25).

Table 25 Variations in the average composition of 8MnO_2 -rich manganese nodules from different areas (from Cronan 1980, Ch. 5, Table 9)

	Mn	Fe	Mn/Fe	Ni	Co	Cu	Pb	Zn
Pacific	15.30	13.78	1.11	0.39	0.79	0.11	0.12	
Atlantic	17.35	21.45	0.81	0.26	0.47	0.08		0.07
Indian	14.7	19.3	0.76	0.25	0.36	0.08	0.14	0.05
LI crusts	20.4	17.3	1.22	0.39	0.55	0.15	0.10	0.06
Penrhyn + Phoenix	17.7	17.0	1.04	0.34	0.34	0.22	0.09	0.06
Todorokite-rich (Mean all oceans)	19.79	11.65	1.70	0.82	0.20	0.47	0.05	0.10

Table 25 shows that the mean Mn/Fe ratio of Pacific 8MnO_2 -rich nodules is greater than either the Atlantic or Indian Ocean nodules. The reason for this is open to question.

Cronan (1975) has forwarded 2 suggestions for the lower Mn/Fe ratios in Atlantic nodules; Firstly, that the Atlantic receives a greater amount of continental runoff products than the other oceans. Since Manheim (1965) has suggested that there is a greater amount of releasable Fe relative to Mn in such products, the inference is that this would tend to decrease the Mn/Fe ratio of nodules. Secondly, many of Cronan's samples came from the mid-Atlantic ridge, leading to the suggestion that there may be an important volcanic source of Fe to the nodules. Furthermore, since Fe (II) oxidises and precipitates more rapidly than Mn on contact with ocean water, one may expect the highest Mn/Fe ratios to occur furthest from continents, assuming no other complicating factors. The LI Archipelago occupies a highly pelagic setting, and the crusts have a mean Mn/Fe = 1.22.

Superimposed on the generally high Mn/Fe ratios are particularly high Mn contents and Mn/Fe ratios in crusts dredged at 1-2 km, coinciding with a dissolved Mn maximum associated with the O₂ minimum (Klinkhammer and Bender (1980). Klinkhammer and Bender (op. cit.) have found that at stations where the oxygen level in the oxygen minimum falls below 100 $\mu\text{mol kg}^{-1}$ ($\approx 2.2 \text{ ml l}^{-1}$) there is a dissolved Mn maximum, and that dissolved Mn contents were particularly high at stations at which the O₂ content was sufficiently low for nitrate reduction to occur ($< 4 \mu\text{mol kg}^{-1}$, $\approx 0.06 \text{ ml l}^{-1}$).

There are 3 models which may explain the Mn maximum:-
 Model 1 - by diffusion from nearshore reducing sediments and advection along isopycnals. The highly pelagic setting of the LI suggests that the model is unlikely to be of importance in this region.
 Model 2 - by regeneration from organic matter through oxidative decay processes.
 Model 3 - by seawater equilibrium with metastable Mn oxides settling through the water column.

Concerning Model 2, both Klinkhammer and Bender (1980) and Landing + Bruland (1980) have used measured Mn/C ratios of plankton coupled to the apparent oxygen utilization

to calculate that oxidative decay can account for the observed Mn maximum in regions where the dissolved O_2 content is between $4 \mu\text{mol kg}^{-1}$ and $100 \mu\text{mol kg}^{-1}$. Furthermore, Klinkhammer and Bender have noted that there is a direct relationship between the apparent oxygen utilization and the Mn concentration in such regions. The model is less satisfactory in regions of nitrate consumption; here insufficient Mn can be supplied by oxidative decay to account for the large Mn maximum (Klinkhammer and Bender 1980). In these cases the higher Mn concentrations may be due to the equilibrium of dissolved Mn and a metastable Mn oxide (Model 3, Klinkhammer and Bender 1980), or, in areas close to continental borderlands, by diffusive/advective transport from anoxic sediments.

Since both Fe oxide and Mn oxide in particular are known to scavenge Mn^{2+} effectively (Stumm and Morgan 1970, Weiss 1977), one may envisage this 'excess' Mn adsorbing onto pre-existing Mn and Fe oxide flocs or directly onto the crusts yielding higher Mn/Fe ratios in crusts at stations at which the O_2 level in the O_2 minimum falls below $100 \mu\text{mol kg}^{-1}$.

The proposed mechanism bears similarities to the mechanism invoked to explain Mn enrichment and increased Mn/Fe ratios in nodules. In the latter the 'excess Mn' is derived either from early diagenetic reactions or by remobilisation of Mn in slightly reducing sediments. There are, however, extremely significant differences between the two cases. Increasing diagenetic influence on the nodules yields higher Mn/Fe ratios and a greater abundance of todorokite. Halbach et al. (1981a) have suggested that Mn/Fe ratios greater than 2.5 are characteristic of todorokite-rich, diagenetically affected nodules, although todorokite is found in nodule exhibiting ratios of less than 2 (Section 12.4). Burns and Burns (1975) have proposed that $5MnO_2$ rather than todorokite occurs in nodules with Mn/Fe ratios approaching unity since $5MnO_2 + FeOOH \cdot xH_2O$ may epitaxially intergrow and physically hinder the development of the todorokite

layer structure. Furthermore Burns and Burns (1977) have pointed out that divalent cations are essential components of the todorokite structure. In terrestrial todorokite these are dominantly Mn^{2+} , whilst in marine todorokites Mn^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} and possibly Mo^{6+} are all found (Arrhenius et al. 1979, Giovanoli and Brüttsch 1979).

In the LI crusts Mn/Fe ratios up to 2.3 are found, and Craig et al. (1982) have measured Mn/Fe ratios up to 4.0 in Hawaiian crusts. All the crusts have a δMnO_2 manganese oxide mineralogy, from which we may reject the hypothesis of Burns and Burns (1975) that the Mn/Fe ratio controls the occurrence of todorokite in ferromanganese deposits. Rather, a lack of divalent transition element cations of suitable size may be the crucial factor in determining mineralogy. Since a supply of Mn (II) to the oxide flocs has been invoked, it must therefore be assumed that the Mn (II) is oxidised on the surface of the flocs to Mn (IV). Morgan (1964), Burns and Brown (1972) and Hem (1977) have suggested that both Mn and Fe oxide can catalyse Mn (II) oxidation.

It should be pointed out that in a closed system, selective reductive dissolution of Mn oxide could lead to a reduction in the Mn/Fe ratio of ferromanganese deposits accreting in that system, contrary to the present observations. Since it has already been suggested that diffusive/advective processes are unlikely to be significant in the LI region, it may be inferred that the 'additional' Mn is derived from oxidative decay. In regions where nitrate reduction appears to be coupled to Mn oxide reduction (Klinkhammer and Bender 1980), dependent on the stability relationships of δMnO_2 one may expect to find ferromanganese crusts with lower than average Mn/Fe ratios.

4.6.4 Element/Manganese Ratios

Mean element/Mn ratios plotted against depth show that elements associated mainly with Mn (Co, Ni, Mo, Cd) are more abundant relative to Mn in crusts from 1-2 km than in deeper crusts (Fig. 29). Pb/Mn shows a similar increase above 3 km depth. Furthermore, regression lines of Co, Mo and Pb versus Mn have negative intercepts on the y axis given by the regression equation (Figs. 3, 4, 9). This may be caused either by a fraction of the total Mn equal to $\left| \frac{\text{intercept}}{\text{slope}} \right| \%$ occurring within a phase devoid of the trace metal, or by a ratio of element/Mn which increases with Mn. For Co, and Mo, plots of Co/Mn and Mo/Mn versus Mn (Figs. 30 a, b) suggest the latter to be the case. Both Co and Mo are strongly associated with Mn. Elements which are associated with both Mn and Fe exhibit positive intercepts when plotted against either Mn or Fe and have decreasing element/Mn ratios with higher Mn values (e.g. Ti, Sr, Figs. 30c and 30d).

The rising manganophile element/Mn ratios with increasing Mn cannot be explained simply in terms of increasing Mn content. Whilst an increasing Mn content will increase the abundance of Mn-associated elements, it will not increase the element/Mn ratios. It is therefore proposed that the crusts are accreting from mixed Mn-Fe oxide flocs rather than separate Fe oxyhydroxide and Mn oxide/oxyhydroxide flocs. As the Mn^{2+} content in the water column rises, adsorption and oxidation of Mn will lead to an increasing proportion of the flocs exhibiting Mn oxide characteristics. This process of 'adsorption and occlusion' will have the effect of increasing both the Mn/Fe ratio and the manganophile element/Mn ratios of the crusts.

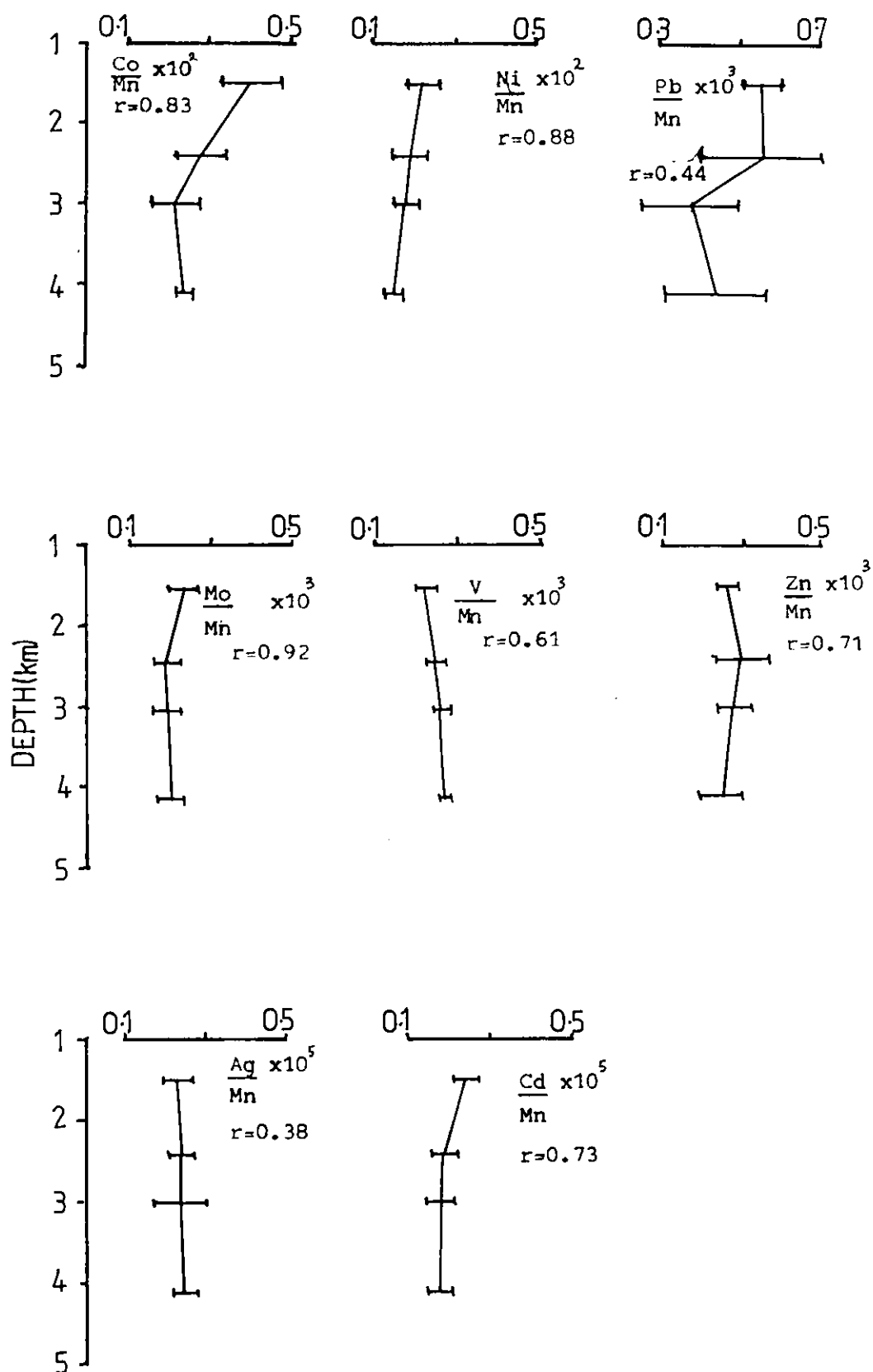


Fig. 29. Depth variations of element/Mn ratios in the LI crusts. r values represent the correlation coefficients between the elements and Mn. Todorokite and goethite bearing samples are not included.

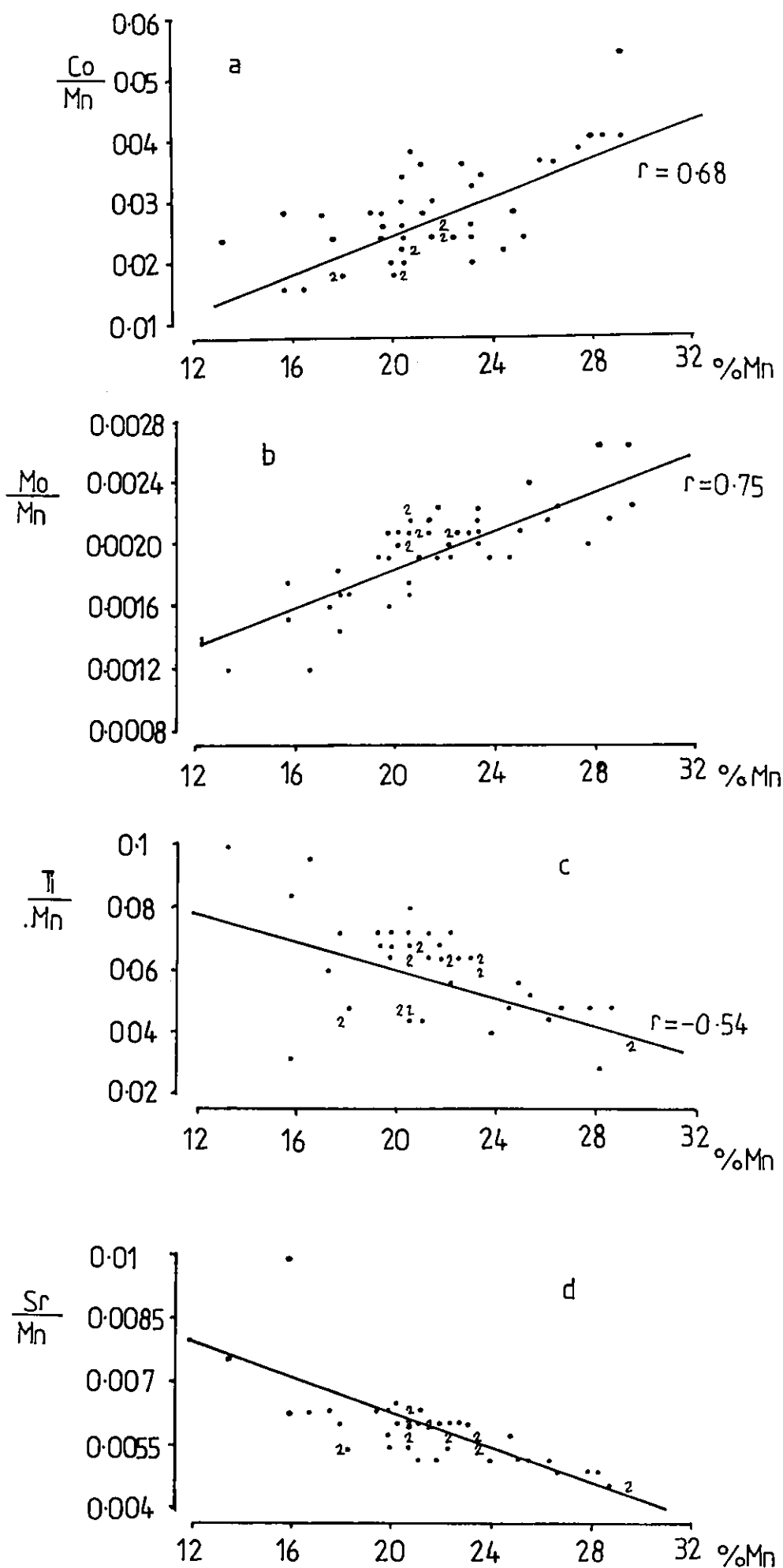


Fig. 30 Plots showing the change in the element/Mn ratios with increasing Mn contents of the crusts.

4.6.5 Cobalt, Lead, Titanium and Cerium

These elements are discussed together since they are all removed from seawater in their higher valence states (Co (III), Pb(IV), Ti(IV) and Ce(IV), Goldberg 1961), implying that they may behave in a geochemically consistent manner which may reflect the Eh of the environment.

Of these elements, Co has received the greatest attention. Both Menard (1964) and Cronan (1967) noted an inverse relation between depth and Co content of nodules, which Cronan interpreted as being due to the higher Eh on sediment-free, current-scoured seamounts. Using a greater data base, Arrhenius et al. (1979) noted that whilst the highest (>1.0%) Co values were found at depths of less than 2000 m, high values (>0.4%, world mean = 0.27%) occur over a wide depth range but are restricted to mainly central Pacific inactive volcanic edifices. They conclude that the high Co content of the nodules is due to weathering of relatively Co-rich pyroclastic debris, with the higher Co contents at shallower depths being due to a more efficient leaching of Co from more porous shallower water eruptives.

The basaltic source of Co may be rejected on several grounds. Firstly, the Co content of weathered basalt is similar to that of fresher material. Secondly, no relationship is seen between substrate type and the Co content of the crusts. Thirdly, most crusts have developed tens of millions of years after the cessation of volcanism, by which time weathering processes will be far advanced. Fourthly, there is no evidence to suggest that the undersides of crusts are Co-enriched with respect to their upper surfaces.

In addition to the high Co Pacific provinces, high Co values are seen in Indian Ocean seamount nodules (0.44%) and Atlantic Ocean seamount nodules (0.54%, Cronan 1980). Furthermore, there is a strong relationship between Co and mineralogy, with Co being enriched in δMnO_2 -rich nodules

and crusts from all oceans (Barnes 1967, Craig et al. 1982, Halbach 1982). A third point is that the LI crusts are Co-enriched compared with nearby SMnO_2 -rich basin nodules (Table 25).

The unifying features of the high Co deposits are their occurrence on seamounts, their SMnO_2 mineralogy and the particularly high Co contents at shallow depths. These features may be explained in terms of the strong affinity of Co to Mn oxide (Murray 1975a, b) and the relative supply of Co and Mn to nodules directly from the water column and from associated sediment. Relative to Mn, the Co content of dispersed oxide material in sediments is depleted compared with encrustations (Section 12.7), which develop directly from the water column. Basin nodules accumulate metals, probably in the form of colloidal oxide flocs, from both sediment and the water column, yielding lower Co contents than in encrustations. On current-swept seamounts, encrustations and nodules are associated with sediment-free zones, thus accumulating metals dominantly from the water column and becoming relatively Co-enriched. The greater Co contents at shallow depths is considered to be due to the greater Mn contents at those depths. Furthermore, the greater Co/Mn ratios observed at shallow depths is due to the enhanced adsorption of Mn onto both Mn and Fe oxide flocs in the O_2 minimum, the subsequent oxidation of Mn and the adsorption of Co by the freshly formed Mn oxide flocs (Section 4.6.4).

It should be noted that within the discussion on Co there is no mention of Eh, since this is a parameter which is virtually impossible to measure both in seawater and, more importantly, at the oxide-seawater interface. It seems likely that the surface chemistry of the oxide phases and the relative affinity of each element for each oxide is an important control on their abundances in the crusts. Murray and Dillard (1979) have calculated that the oxidation of Co (II) to Co (III) and Pb (II) to Pb (IV) on the surface of MnO_2 is thermodynamically possible. Using X-ray photoelectron spectroscopy, the oxidation

of Co has been experimentally verified (Murray and Dillard 1979), and the existence of Co (III), Pb (IV) and also Pb (II) in Mn nodules has been shown. The occurrence of both Pb (II) and Pb (IV) in nodules may reflect the adsorption of Pb onto both Fe oxides and Mn oxides (Kinniburgh et al. 1976, Murray 1975a), with subsequent oxidation only in the presence of the strong electric field at the MnO_2 -solution interface (Murray and Dillard 1979).

The fractionation of Ce from the other trivalent rare earth elements, which is observed as a negative anomaly in seawater and a positive anomaly in ferromanganese deposits, is commonly ascribed to its occurrence in seawater in the tetravalent state. Tentatively extrapolating the Ce speciation data of Pourbaix (1974) in the aqueous system at 25°C , the likely dissolved species are Ce^{3+} and $\text{Ce}(\text{OH})_2^{2+}$; other REE will not occur as the latter, suggesting that the Ce enrichment in the crusts is a function of differential adsorption of $\text{Ce}(\text{OH})_2^{2+}$ or the formation of a solid solution series with Mn and/or Fe oxyhydroxides.

Similarly, Pourbaix's (1974) data suggests that $\text{TiO}_2 \cdot \text{H}_2\text{O}$ should be the most stable species in seawater. Rather than inferring coprecipitation reactions between Fe and Ti resulting in the formation of Fe-Ti oxides (Ruppert 1980), it is suggested that TiO_2 may accumulate with both Mn and Fe oxides, or independently of both, which would explain the lack of an Fe-Ti relationship commonly observed in nodules (Goldberg 1954, Cronan 1967).

4.7 Comparison of the LI crusts with other ferromanganese crusts

Two other studies of Pacific ferromanganese crusts have recently been published. Firstly, Craig et al. (1982) have reported on a suite of crusts dredged between 800 m and 2000m in the Hawaiian Archipelago, and secondly Friedrich and Schmitz-Wiechowski (1980) have reported the chemistry and mineralogy of a thick encrustation dredged at 4,830 m

in the Central Pacific. Details of their mean element abundances are given in Table 26.

Table 26 Mean chemical compositions of LI crusts,
Hawaiian crusts, central Pacific crust and
Penrhyn Basin/Phoenix Is. δMnO_2 -rich nodules

	No. of samples	Mn	Fe	Ni	Co	Co/Mn	Ni/Mn	Mn/Fe
Line 1 Islands	59	20.4	17.3	0.39	0.55	0.027	0.019	1.11
Hawaiian ²	47	21.8	15.8	0.42	0.80	0.037	0.019	1.63
Central Pacific ³	19	20.0	25.4	0.27	0.17	0.009	0.014	0.79
Penrhyn/ ¹ Phoenix nodules	23	17.7	17.0	0.34	0.34	0.019	0.019	1.04

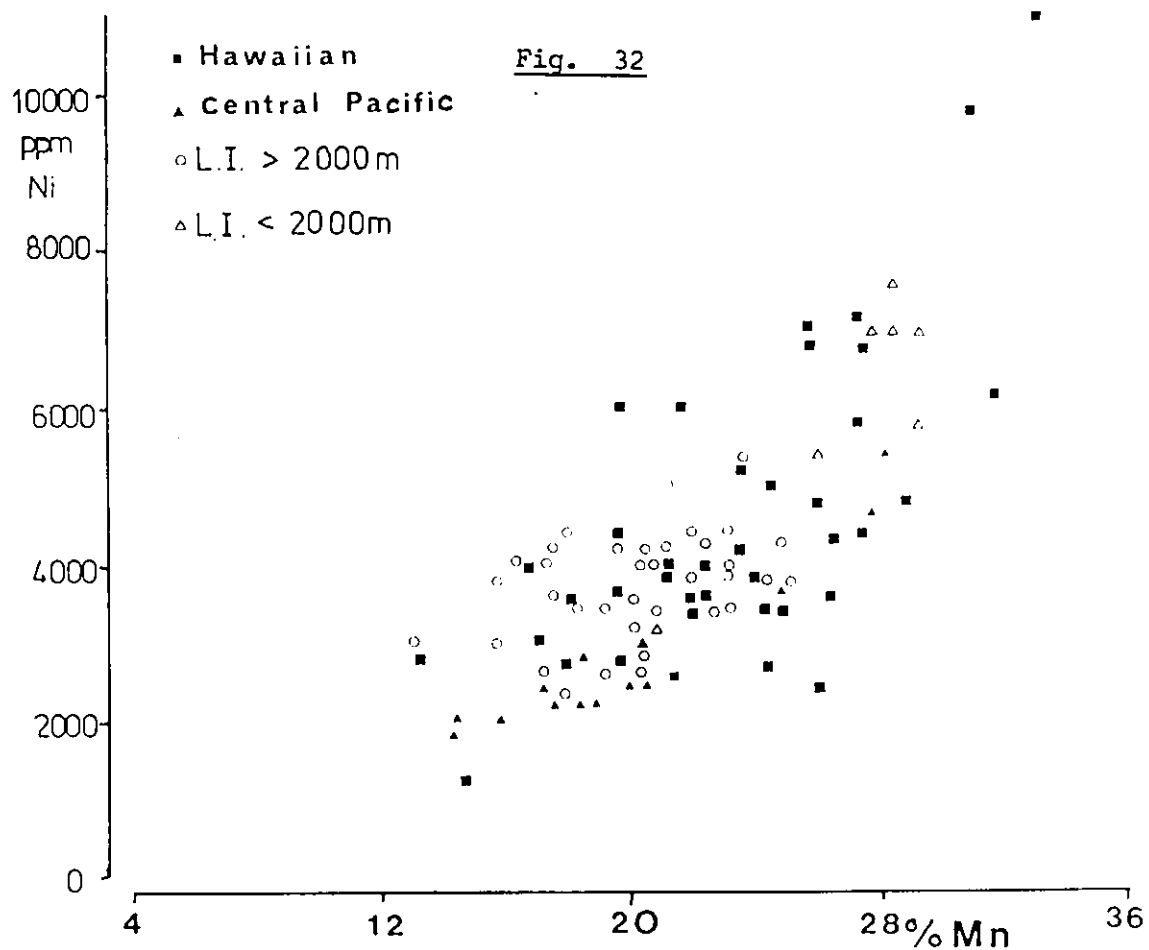
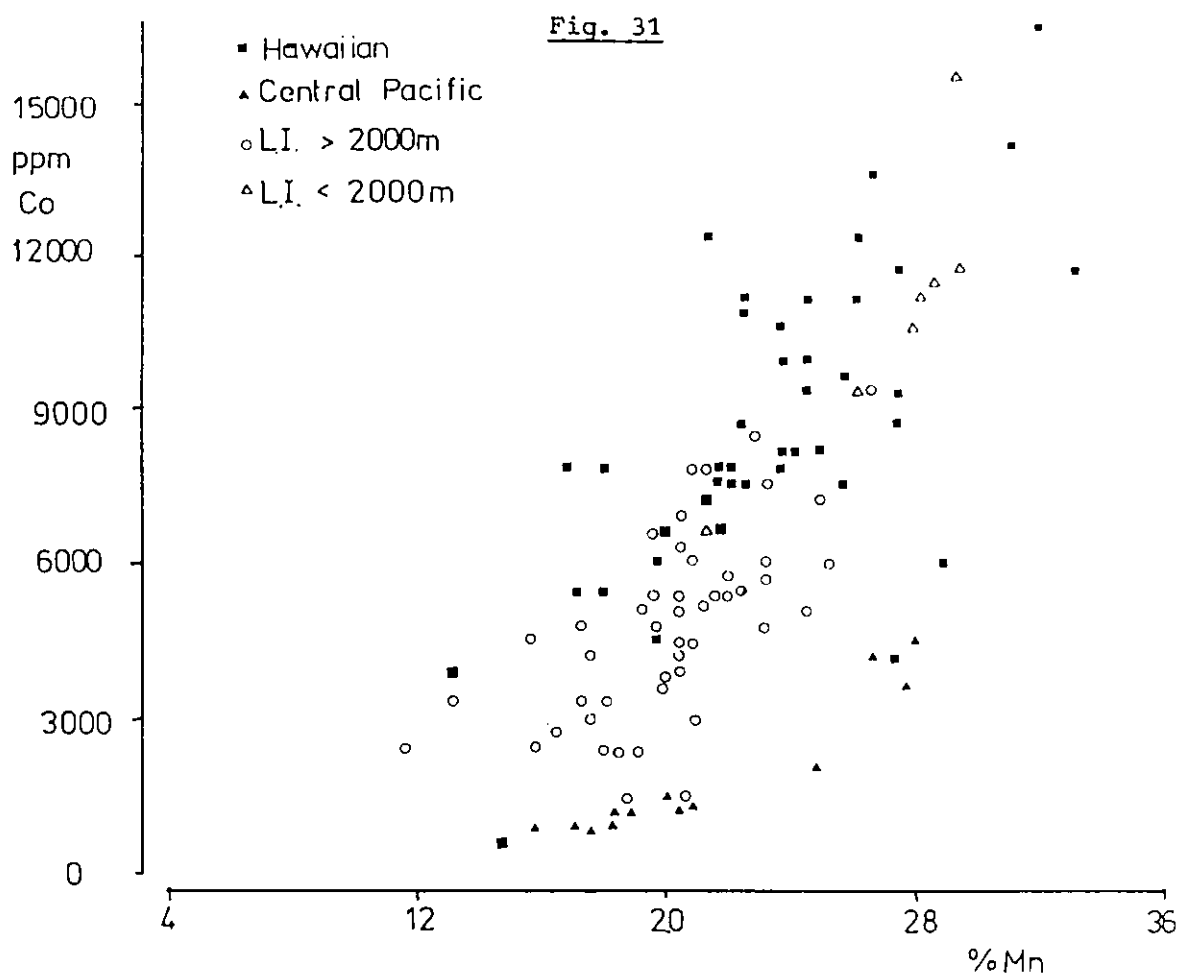
¹ data from this study

² data from Craig et al. (1982)

³ data from Friedrich and Schmitz-Wiechowski (1980)

Combined plots of Co versus Mn and Ni versus Mn for the LI, Hawaiian and Central Pacific crusts are shown in Figs. 31 and 32. The Hawaiian crusts plot in the same region as the shallow LI crusts. The mean Mn/Fe ratio of the Hawaiian crusts is 1.63 ($s = 0.79$) compared to 1.90 ($s = 0.50$) for the <2000 m LI crusts and 1.11 ($s = 0.18$) for the >2000 m LI crusts. The Central Pacific crust, although it too shows strong Mn:Ni and Mn:Co correlations, is deficient in both elements, especially Co. In addition, it has a low mean Mn/Fe ratio.

Clearly the Hawaiian crusts, whilst exhibiting important variability, are genetically related to the shallow LI crusts. The lower Mn/Fe, Ni/Mn and Co/Mn ratios of the Central Pacific crust are less easy to explain. One possibility is that the crust is accreting from metals diffusing out of nearby sediment in response to early diagenetic reactions. Mn, Cu and Ni are known to take part in these, whilst Co does not (Klinkhammer 1980).



Figs. 31+32 Ni,Co versus Mn plots for Pacific Fe-Mn encrustations. Data from this work, Craig et al. (1982), Friedrich and Schmitz-Wiechowski (1980).

This would explain the greater depletion of Co relative to Ni and Cu, but neither the low Mn/Fe ratio nor the low Ni/Mn ratio. It is interesting to note that Ce, which like Co does not take part in early diagenetic reactions (Elderfield et al. 1981), is generally depleted in the central Pacific crust over the LI crusts.

4.8 Dissolved oxygen

Previous discussions have indicated that the Mn/Fe ratio exerts a considerable influence on crust chemistry and that the higher Mn/Fe ratios are associated with waters enriched in Mn possibly by oxidative decay in waters containing between $4 \mu \text{mol kg}^{-1}$ ($\approx 0.09 \text{ ml l}^{-1}$) and $100 \mu \text{mol kg}^{-1}$ ($\approx 2.2 \text{ ml l}^{-1}$) dissolved oxygen. Areas where dissolved O_2 falls below $4 \mu \text{mol kg}^{-1}$ may contain crusts with lower than average Mn/Fe ratios. Delineation of those areas of the ocean in which dissolved oxygen is present in $4 - 100 \mu \text{mol kg}^{-1}$ concentrations might enable prediction of where the Mn/Fe ratio is likely to be high and thus where the abundances of the economically important elements Co and Ni are likely to be highest.

The level of dissolved O_2 in an open ocean water mass is a function of its supply by advective thermohaline currents and its utilisation by biochemical processes. Most intermediate and deep water masses are formed at the ocean surface where they become saturated with O_2 . As they sink, O_2 is utilised in biochemical processes. Thus sluggish currents at great distances from their source and under regions of high biological productivity tend to have reduced O_2 contents.

Overall, Wyrski (1962) has suggested that the general distribution of O_2 in the oceans is consistent with the deep circulation pattern (Stommel 1958). Thus large bodies of water of extremely low O_2 content are found on the eastern side of the oceans, in subtropical regions, where intermediate and deep waters are old and sluggish and where biological productivity is moderately high (Reid 1962). The younger water masses of the Atlantic Ocean are overall richer in O_2 compared to the Pacific Ocean,

and values of less than 3 ml l^{-1} are rare.

Because Pacific intermediate and deep currents flow predominantly northwards, the north Pacific is O_2 depleted relative to the South Pacific (Fig. 33). Particularly, Antarctic Intermediate Water, which forms at 50°S at the Antarctic Convergence, is relatively rich in O_2 and flows north as far as the equator. Values of dissolved O_2 of less than 2.2 ml l^{-1} are rare south of 20°S , whilst in the north Pacific such values may extend between 300 + 3,000 m (Fig. 33).

Over much of the Pacific an oxygen minimum layer develops centred between 200 and 1,200 m in response to the oxidative decay of biological material. Below this level the O_2 content of the water increases gradually (Fig. 28). Clearly the more intense is the minimum, the greater will be the depth range over which O_2 levels will be below $100 \mu \text{ mol kg}^{-1}$. Recent dissolved O_2 profiles (e.g. Edmond 1974, Klinkhammer and Bender 1980) support these generalisations: for example a profile at 18°N 169°W , shows dissolved O_2 levels of less than $100 \mu \text{ mol kg}^{-1}$ between 500 and 2000 m (Edmond 1974).

One would therefore predict a greater probability of finding high Mn/Fe, high Co + Ni crusts in the Pacific Ocean north of 20°S and at depths between approximately 300 - 500 m and 2500 m. This is supported by the LI and Hawaiian data. However, a cautionary note must be added; although relatively little is known about the small-scale variability of dissolved O_2 , it may be expected to vary according to local environmental conditions. Currents in complex seamount topography are unpredictable in both speed and direction, and local upwelling/downwelling may occur. Mao and Yoshida (1961) have studied the distribution of dissolved O_2 between 3°S and 20°N , 160°E - 175°E in some detail. They found significant variations in the intensity of the O_2 minimum and its horizontal distribution. The lower O_2 concentrations were found in areas of large horizontal surface eddies between $4 + 10^\circ\text{N}$ and were explained

in terms of high stability at the bottom of the isothermal layer preventing effective transport of O_2 below the mixed layer.

Such regional and local variability in the O_2 distribution may explain the variability in the Mn/Fe ratios of the Hawaiian crusts, which are all dredged at depths at which the O_2 content may be expected to be low.

Thus in a similar way to the direction of nodule research - first an examination of large-scale variability followed by an analysis of local variability - it would be of great interest now to look at the local factors which may control the chemistry of the crusts.

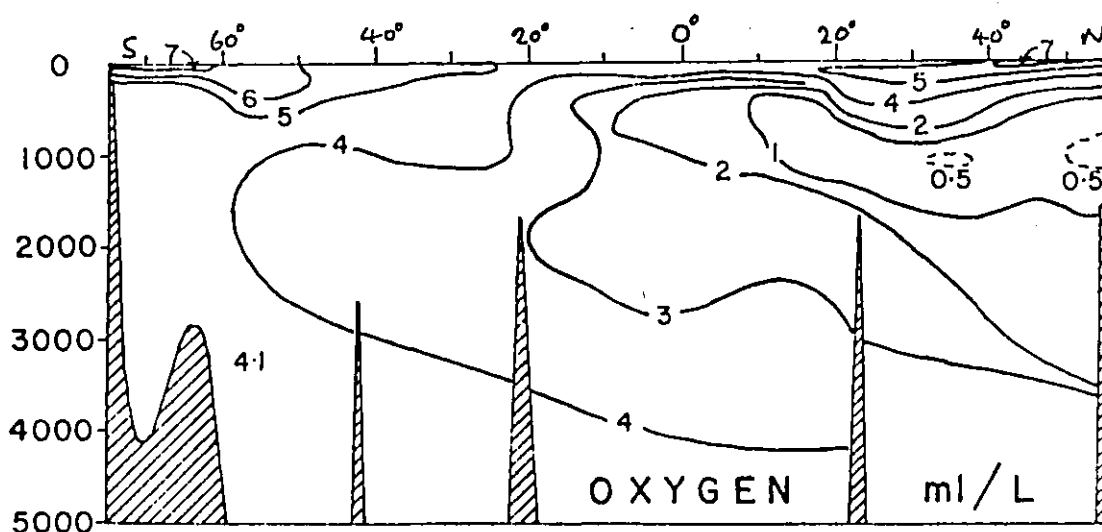


Fig. 33 South-north longitudinal sections of water characteristics in the Pacific Ocean along $175^{\circ}W$ (from Pickard 1975).

CHAPTER 5 THE REE GEOCHEMISTRY OF THE LINE ISLANDS CRUSTS

5.1 Introduction

In the last ten years there has been a considerable upsurge of interest in the marine geochemistry of the rare earth elements (REE). This is due to the interesting chemistry of the group coupled with the development of more rapid and precise analytical techniques. The salient points of their chemistry, which has been summarized concisely by Elderfield and Greaves (1982), are as follows:-

1. They are an extremely coherent group which precludes their extensive fractionation through the geochemical cycle and allowing inferences to be made on their source in a sedimentary deposit. (Bender et al. 1971, Piper 1974a, Piper and Graef 1974). Thus both absolute and relative abundances are of potential importance.
2. Whilst most REE exist in the trivalent state, Ce can exist both as Ce(III) and Ce(IV) and Eu as Eu(II) and Eu(III). Each may therefore fractionate from the trivalent REE as a function of redox potential.
3. The stability constants of the REE with seawater ligands increases with atomic weight. Goldberg et al. (1963) have suggested that this, coupled with differential scavenging by solid phases, can explain the characteristic heavy REE-enriched pattern of seawater.
4. The radioactive decay of ^{147}Sm to ^{143}Nd plus the fractionation of Sm from Nd between continental crust and mantle means that the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio may be used to examine the sources of the REE in a sedimentary deposit. Recent work by O'Nions et al. (1978), Piepgrass et al. (1979) and Elderfield et al. (1981a) has addressed this problem in the marine environment.

Recent work on the REE geochemistry of ferromanganese nodules has been reported by Glasby (1973b), Piper (1974b),

Addy (1979), Rankin and Glasby (1979), Courtois and Clauer (1980), Elderfield et al. (1981a, b) and Elderfield and Greaves (1981). Working on a small suite of diagenetically influenced nodules, the transition element geochemistry of which was well documented by Calvert et al. (1978), Elderfield et al. (1981a) proposed that early diagenetic reactions which enrich nodules in the transition elements Cu, Ni, Zn and Mo and increase the Mn/Fe ratio tend to deplete them in the REE. The REE contents are controlled by a P-rich phase with a REE pattern similar to that of biogenous apatite and an Fe-rich phase with a REE pattern the mirror-image of that for seawater. The 3+ REE concentrations are controlled by the surface chemistry of these phases during diagenetic reactions. Ce, on the other hand, showed dissimilar behaviour to the 3+ REE and was interpreted to be added to the nodules directly from seawater.

The Line Islands crusts represent a closely controlled suite of 8MnO_2 -rich, hydrogenous ferromanganese crusts, the transition element chemistry of which is known (Chapters 3 & 4). The REE chemistry of such material has not been reported previously, and stands in comparison with and as a corollary to the todorokite-rich, diagenetically influenced nodules reported by Elderfield et al. (1981a, b).

5.2 Absolute REE abundances

The REE abundances of the crusts are given in Table 27, and the mean, standard deviation and coefficient of variation of each element in Table 28.

Concentrations are higher than those reported by Elderfield et al. (1981a), in keeping with their conclusion that early diagenetic reactions within the sediment reduce the abundances of the REE in associated nodules. However, concentrations are not uniformly higher in the crusts (Table 29). La and Ce are most strikingly enriched, whilst the heavy REE show greater enrichment factors than the intermediate REE. Furthermore, whilst the coefficients

Table 27 REE and selected transition element abundances in the LI Crusts

REE, Ti, Co, Pb in ppm Mn, Fe in wt.%

	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu	Mn	Fe	Ti	Co	Pb
041 1/1	175	611	25.8	131	25.6	6.74	30.6	34.4	8.20	25.6	23.7	3.72	29.30	14.36	10600	11600	1601
044 2/2	218	496	32.4	160	30.0	7.82	35.2	39.6	9.32	28.32	26.2	4.02	26.10	18.30	11800	9300	1372
045 6/13B	165	712	21.6	109	18.8	5.28	24.2	27.9	6.99	22.0	21.1	3.36	27.60	13.74	13800	10500	1331
050 4/6A	387	1445	65.4	294	67.2	16.58	69.6	59.7	12.40	34.8	33.8	5.50	25.00	19.80	12800	6000	855
050 4/6B	276	895	54.6	255	53.4	12.60	53.2	51.7	10.74	31.7	27.5	4.28	20.60	18.52	9100	4600	703
051 6/7A	139	324	23.6	113	21.2	5.24	22.6	24.4	5.16	16.3	14.2	2.16	17.60	15.76	8000	3090	458
053 1/1D	228	219	43.4	201	47.8	11.98	55.8	50.0	10.78	31.0	28.9	4.68	8.39	6.24	4610	1070	165
055 3/3	172	298	28.0	139	27.0	7.04	30.6	32.0	7.26	20.9	19.0	2.92	15.40	16.10	5130	2320	313
058 1/2	330	935	64.0	301	63.4	15.76	65.6	60.1	11.94	33.3	28.5	4.28	21.60	21.00	3900	6600	1356
058 2/2B	223	1143	30.1	158	29.8	7.62	36.0	39.5	9.54	31.0	27.0	4.32	27.90	12.30	7700	11200	1556
059 7/7	344	1262	77.6	360	76.3	18.55	73.2	67.8	12.95	35.8	29.5	4.25	20.30	19.50	14800	5470	1234
060 2/4B	332	1038	69.8	327	68.0	16.74	68.4	65.6	13.06	36.6	30.9	4.54	20.30	18.21	12600	4960	1115
061 2/5	306	997	58.8	275	57.2	14.32	58.6	55.8	11.42	32.1	28.7	4.28	21.90	19.00	12000	5400	930
062 1/3A	295	701	58.2	269	53.8	13.06	54.0	52.3	10.80	30.9	27.3	4.06	20.80	18.46	13800	4640	1004
062 1/3D	316	1459	56.6	257	47.4	11.16	42.0	38.0	7.70	21.4	18.4	2.80	18.50	20.62	14300	2380	1363
062 1/3F	461	2916	58.0	281	55.6	13.90	59.6	48.3	10.14	29.8	26.5	4.34	18.00	19.62	17400	2440	2374
063 2/9A	306	894	53.8	258	49.6	12.36	53.8	54.9	11.86	34.3	29.8	4.40	24.70	16.27	13700	7100	1471
063 5/9A	350	991	65.2	309	62.9	15.73	66.7	63.3	12.85	36.4	31.4	4.66	21.00	21.90	15200	6000	1406
064 5/7B	351	1146	70.2	331	77.0	16.48	68.2	65.9	13.30	37.9	32.0	4.84	20.60	20.80	13700	7700	1438

Table 28 Means, standard deviations and coefficients
of variation of REE concentrations of Line
Islands crusts, nodules from Piper (1974b)
and todorokite-rich nodules from Elderfield
et al. (1981a)

Line Islands crusts				Piper (1974b)			Elderfield et al. (1981a)		
No. of samples 19				36			8		
	$\bar{X}$	s	CV(%)	$\bar{X}$	s	CV(%)	$\bar{X}$	s	CV(%)
La	283	86	30	220	113	51	102	27	26
Ce	972	594	61	667	467	70	435	225	52
Pr	50.4	18.0	36						
Nd	238	80	34	230	132	57	145	37	26
Sm	49.2	18.8	38	44	22	50	24.4	9.0	26
Eu	12.05	4.25	35	9.6	4.5	47	8.16	1.92	24
Gd	50.9	16.6	33				33.3	8.7	26
Dy	49.0	13.6	28				30.3	7.2	24
Ho	10.34	2.37	23						
Er	30.0	6.1	20				16.1	4.1	25
Yb	26.5	5.1	19	20	11	55	14.8	3.9	26
Lu	4.07	0.78	19	3.4	1.9	56			

Table 29 Enrichment factors of Line Islands crusts over
todorokite-rich nodules^a & Bauer Basin ferro-
manganese crusts^b

	Todorokite-rich nodules	Bauer Basin Crust
La	2.8	2.3
Ce	2.2	7.9
Nd	1.6	2.4
Sm	1.4	2.5
Eu	1.5	2.2
Ed	1.5	2.0
Dy	1.6	1.9
Er	1.9	1.8
Yb	1.8	1.7

^a data from Elderfield et al. (1981a)

^b data from Elderfield + Greaves (1981)

of variation of the 3+ REE are almost constant in the diagenetically influenced nodules, they differ significantly in the crusts.

Piper's (1974b) results are much closer to those found in this study; like the LI crusts many of the nodules in that study contained SMnO_2 as the main Mn oxide mineral, indicative of the lack of diagenetic influence (Price and Calvert 1970, Calvert and Price 1977).

The crusts are also enriched in REE over a Bauer Basin crust (Table 29) which is considered to contain a hydrothermal component of Fe oxyhydroxide derived from the East Pacific Rise and associated REE from the water column (Elderfield and Greaves 1981). Aside from Ce, which is greatly enriched, enrichment is greatest for Nd and Sm and declining towards both light and heavy ends.

The lowest abundances of REE occur in samples O51 6/7A, O53 1/1D and O55 3/3. O51 6/7A + O53 1/1D exhibit high Al contents + O55 3/3 a high Ca content. X-ray diffractograms of residues of these crusts leached by acidified hydroxylamine hydrochloride (Chester and Hughes 1967) indicate that the Al in O51 6/7A and O53 1/1D is due to the presence of phillipsite.

The high Ca in O55 3/3 is due to francolite contamination. These phases are known to have widely different absolute and relative concentrations of REE to ferromanganese oxides (Piper 1974a) and are not considered in following discussions. On the other hand, O58 2/2B also has a high (5.1%) Ca content, but still has a high REE content and will be used in the discussion.

5.3 Relative REE abundances

In addition to variations in absolute abundances, Fig. 34 indicates that the relative abundances of the REE also vary. This is in contrast to the findings of Elderfield et al. (1981a) who determined that whilst absolute concentrations of the 3+ REE varied, relative concentrations were almost identical. The REE correlation

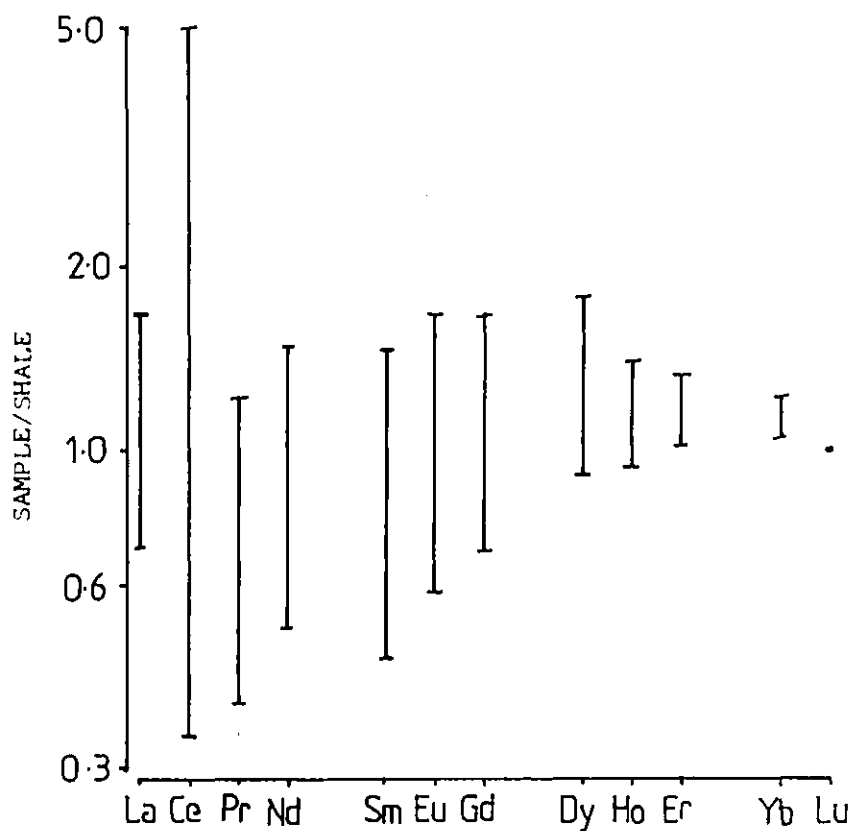


Fig.34 Ranges of REE in the LI crusts,normalised to shale and Lu=1.

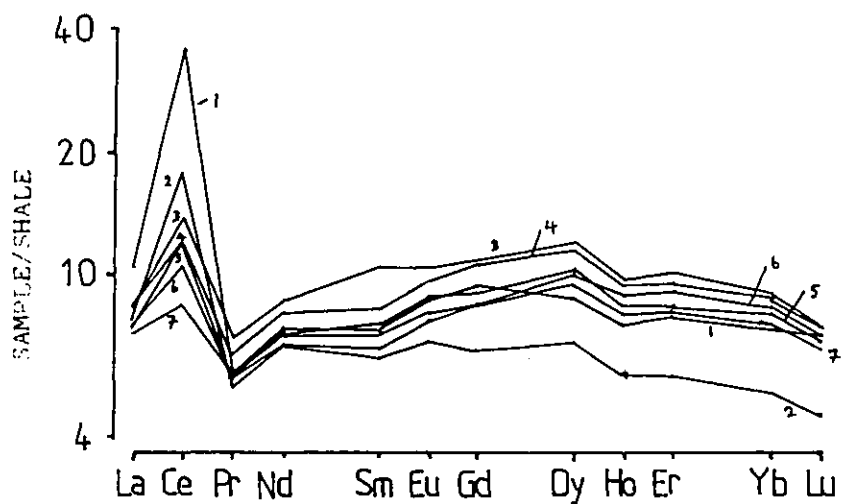


Fig. 35 Shale normalised REE patterns of LI crusts.

- | | |
|-------------|-------------|
| 1- 062 1/3F | 5- 061 2/5A |
| 2- 062 1/3D | 6- 063 2/9A |
| 3- 064 5/7B | 7- 062 1/3A |
| 4- 063 5/9A | |

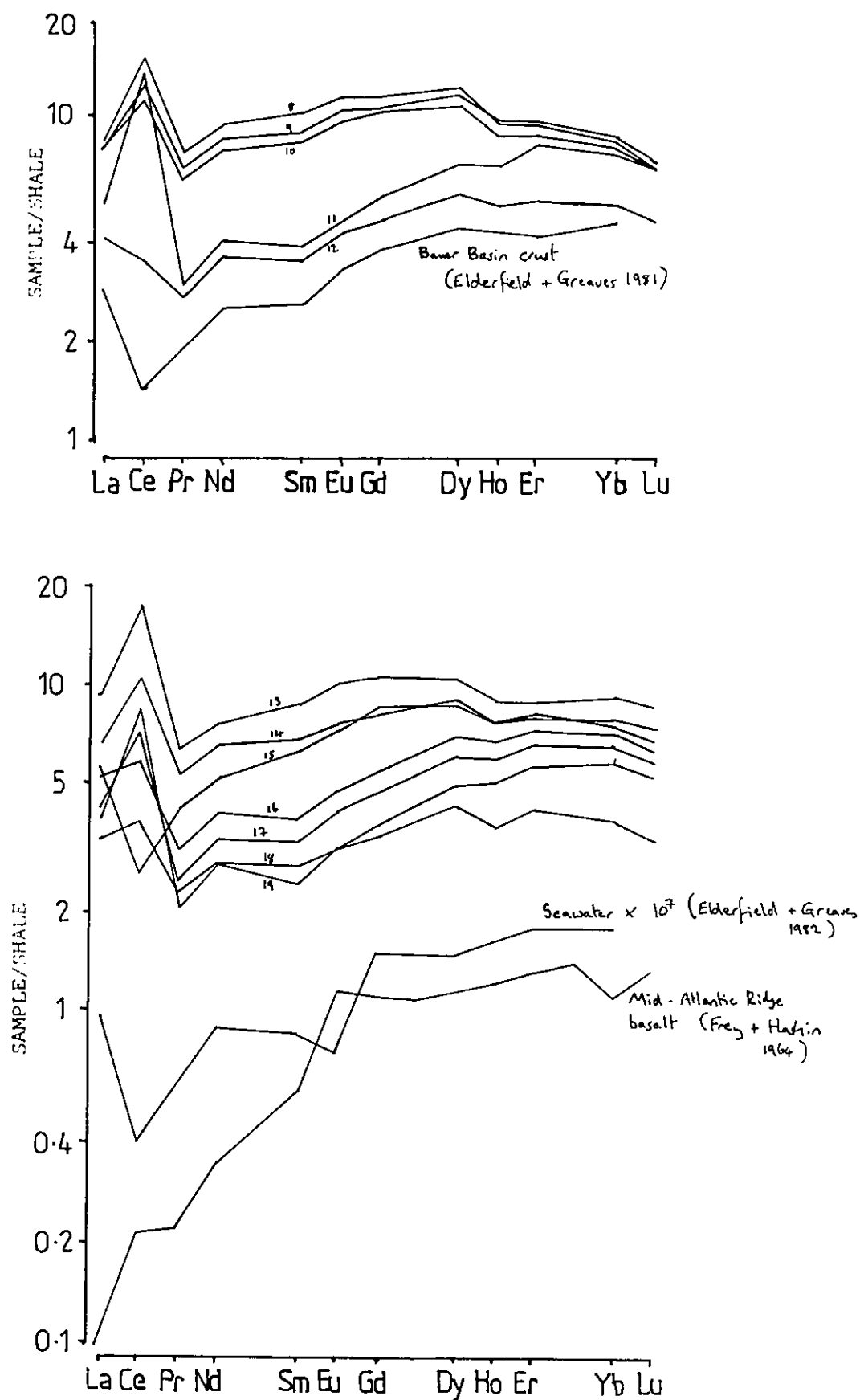


Fig. 35 (cont.)

8- 059 7/7
 9- 060 2/4B
 10- 058 1/2
 11- 058 2/2B
 12- 055 3/3

13- 050 4/6A
 14- 050 4/6B
 15- 053 1/1D
 16- 044 1/1
 17- 041 1/1

18- 045 6/13B
 19- 051 6/7A

matrix (Table 30) shows that for the 3+ REE the closer within the periodic table the elements are the more coherent is their geochemical behaviour in the crusts. Ce is poorly correlated with all the REE.

5.4 Incorporation of the REE in the crusts

The exceptionally close $^{143}\text{Nd}/^{144}\text{Nd}$ ratios determined for Pacific seawater (Piepgrass et al. 1979), nodules (O'Nions et al. 1978, Piepgrass et al. 1979, Elderfield et al. 1981 and East Pacific Rise metalliferous sediment (O'Nions et al. 1978) points to an original seawater source for the REE in these deposits.

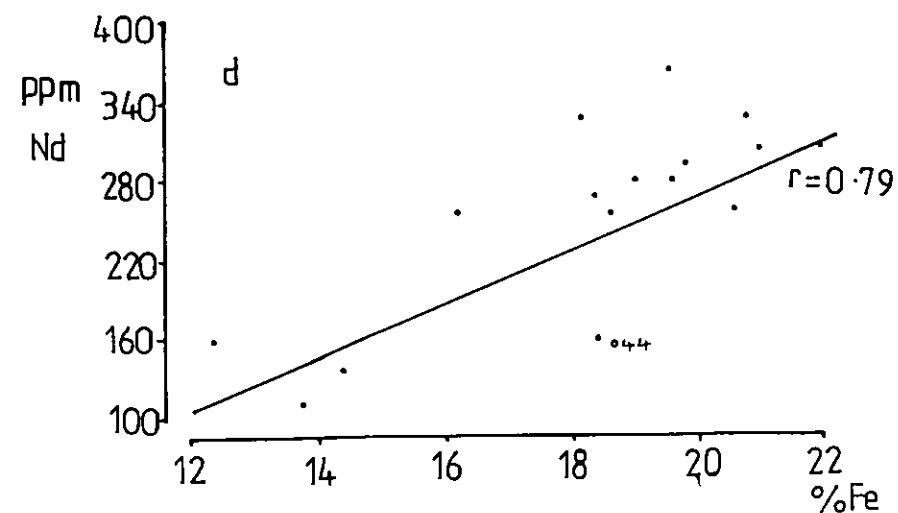
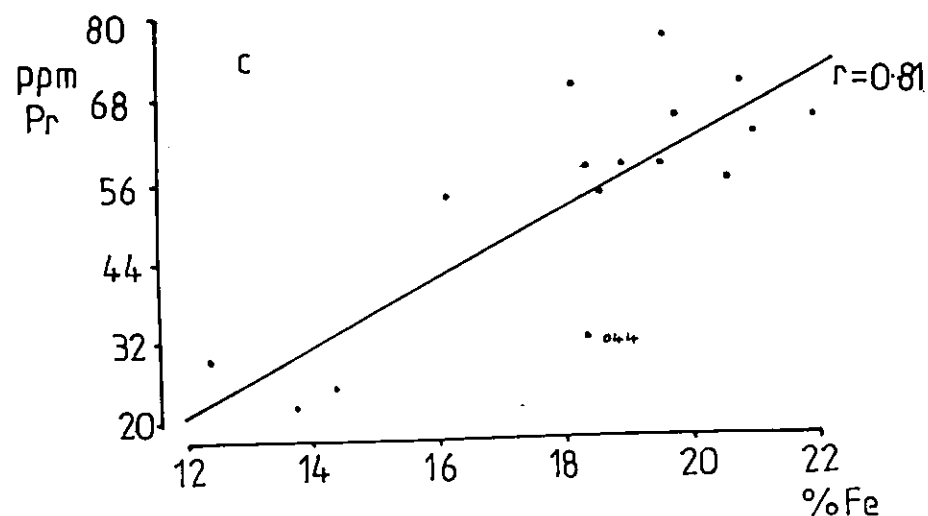
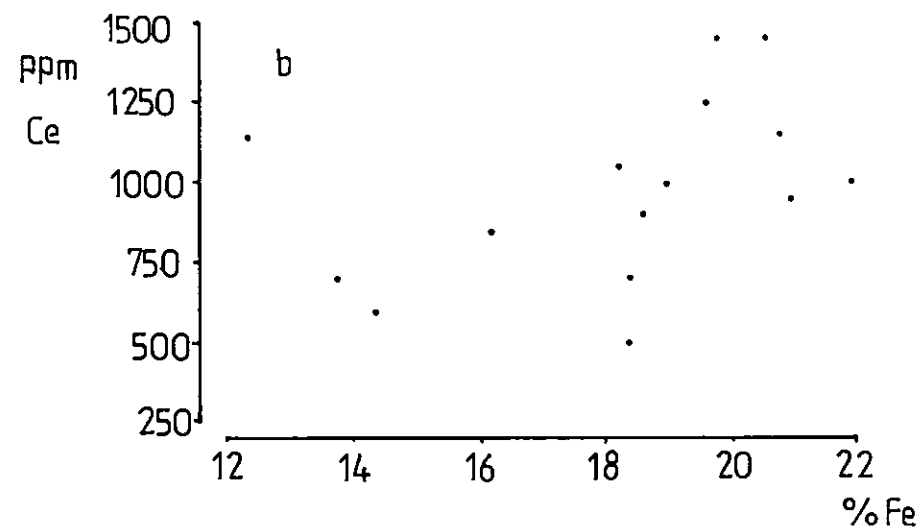
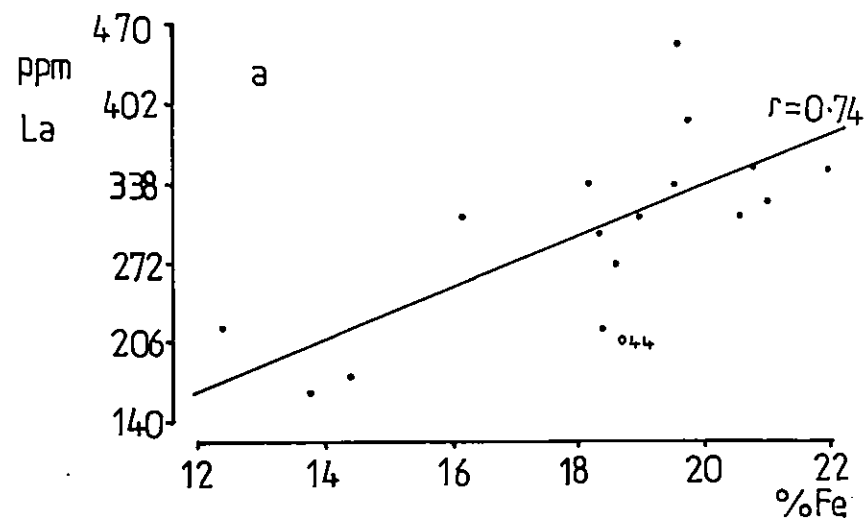
Although there is no Nd isotope data for the crusts, the general similarity of the REE pattern with that of nodules and the obvious dissimilarity with that of oceanic basalt (Frey and Haskin 1964, Fig. 35) precludes halmyrolysis as an immediate source for the REE and indicates a seawater source. However, direct precipitation from seawater is untenable since the 3+ REE are undersaturated with respect to likely salts. (Turner and Whitfield 1979).

Scavenging by the Mn and Fe oxyhydroxide flocs is the most likely method for incorporation of the REE. Scatter plots of individual REE versus Fe (Figs. 36a-36l) coupled with the correlation data (Table 30) indicate that a strong relation exists between Fe and the light and intermediate REE, (except Ce) but decreasing steadily along the heavy REE, particularly for elements heavier than Gd. Concomitantly there is a decrease in the negative correlation with Mn, with the heavy REE accumulating almost independently of Mn or Fe. Elderfield et al. (1981a) determined that an Fe-rich phase and a P-rich phase controlled the REE geochemistry of diagenetically influenced nodules. For the crusts, no relation can be seen between any REE and P (Fig. 37), or indeed between Fe and P. However, because the regression lines for Ho, Er, Yb and Lu versus Fe have positive intercepts, (Figs. 36i - 36l), these elements at least are partly

Table 30 REE correlation matrix, omitting O51 6/7A, O53 1/1D and O55 3/3

	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu	Mn
Ce	0.76												
Pr	0.83	0.34											
Nd	0.84	0.36	1.00										
Sm	0.81	0.33	0.98	0.99									
Eu	0.83	0.34	0.98	0.98	0.99								
Gd	0.83	0.34	0.96	0.97	0.98	0.99							
Dy	0.69	0.14	0.92	0.93	0.95	0.96	0.97						
Ho	0.64	0.09	0.84	0.85	0.89	0.89	0.93	0.98					
Er	0.55	0.05	0.72	0.74	0.79	0.79	0.84	0.92	0.98				
Yb	0.52	0.04	0.62	0.64	0.71	0.72	0.79	0.84	0.92	0.96			
Lu	0.52	0.16	0.49	0.50	0.59	0.61	0.69	0.70	0.80	0.85	0.96		
Mn	-0.77	-0.53	-0.80	-0.80	-0.73	-0.72	-0.67	-0.57	-0.44	-0.31	-0.5	-0.5	
Fe	0.74	0.30	0.81	0.79	0.78	0.77	0.74	0.66	0.56	0.42	0.37	0.28	-0.79

n = 19
r = 0.57 is significant at the 99% confidence level



Figs. 36a-1 Scatter plots of individual REE vs. Fe in the LI crusts. D,F refer to crust 062 1/3. Plots do not include the francolite or phillipsite contaminated samples 053 and 055.

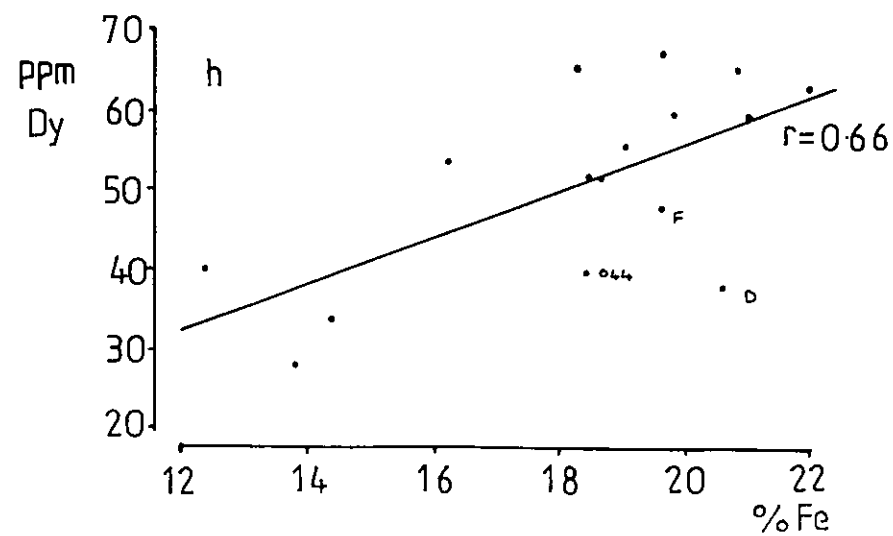
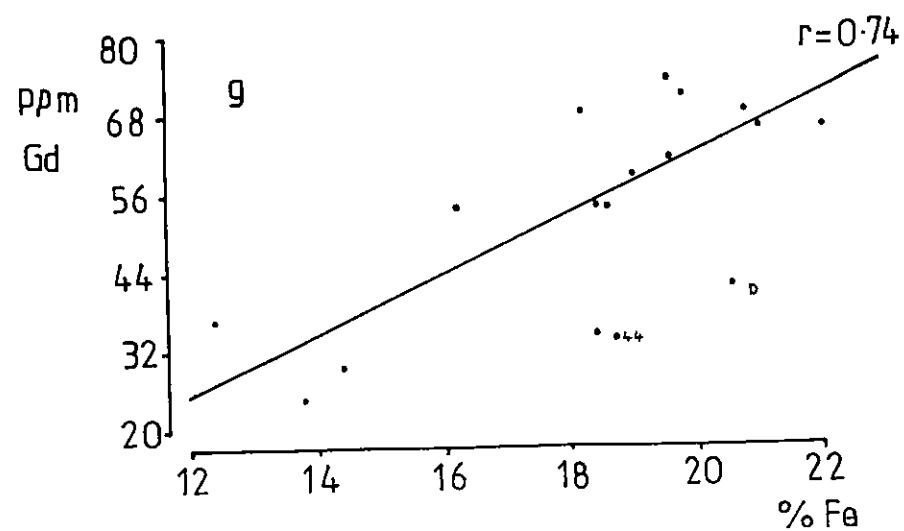
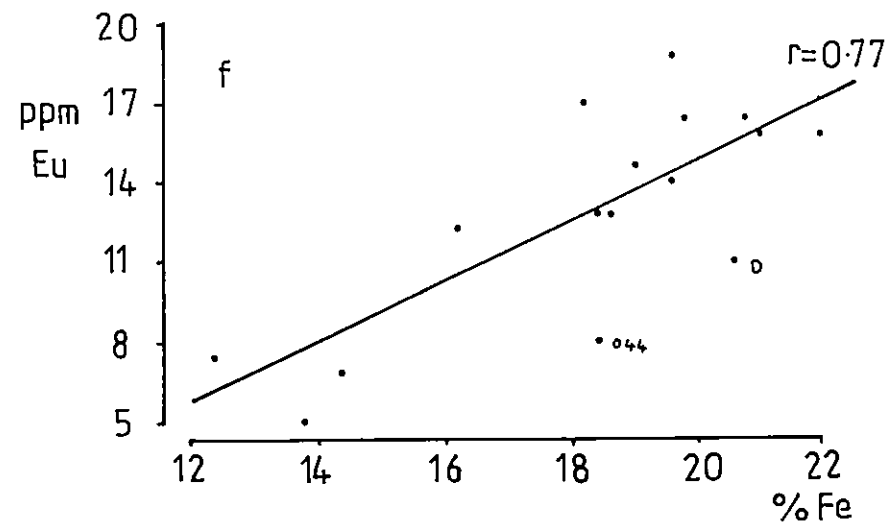
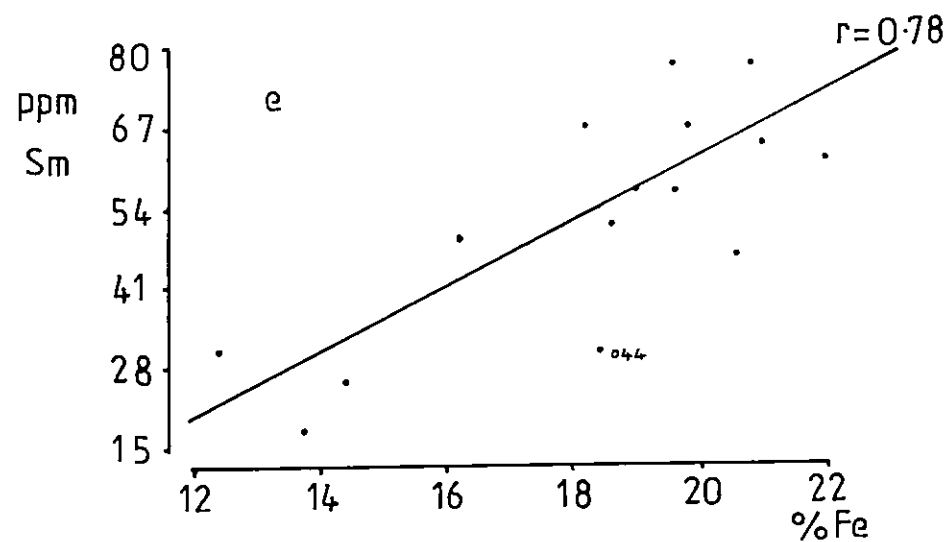


Fig. 36 (cont.)

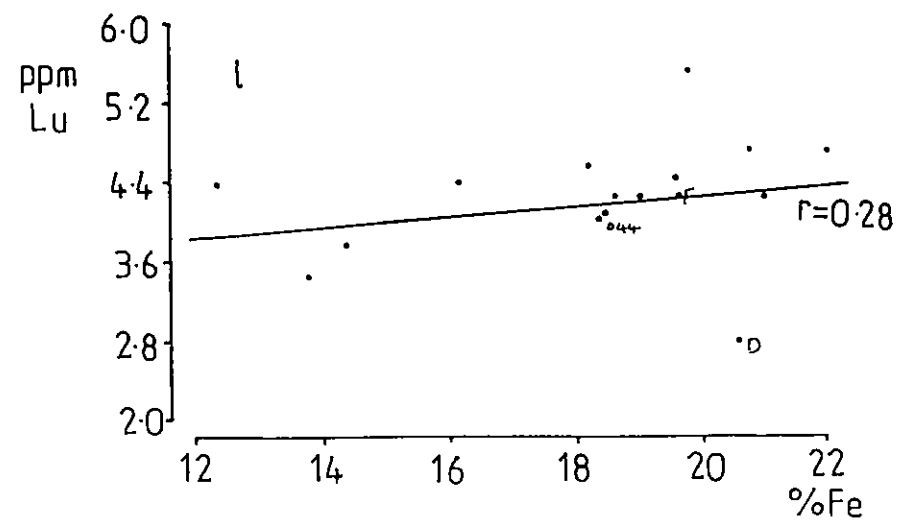
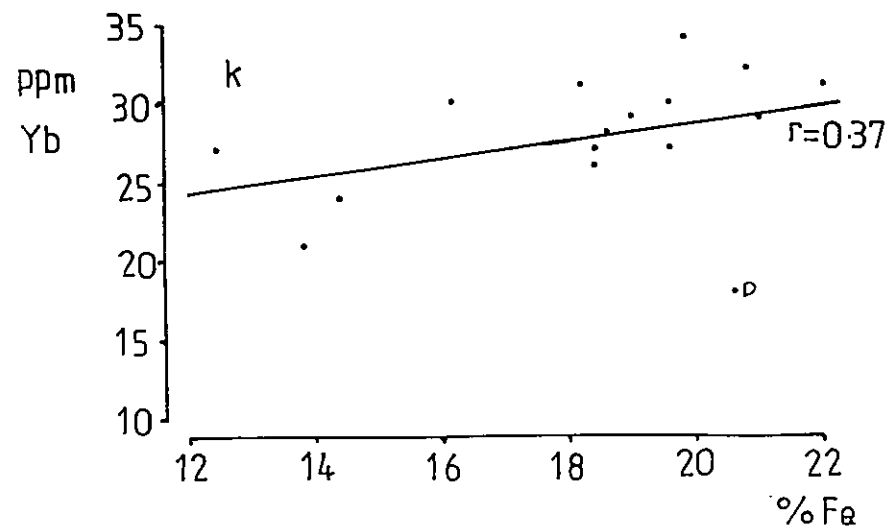
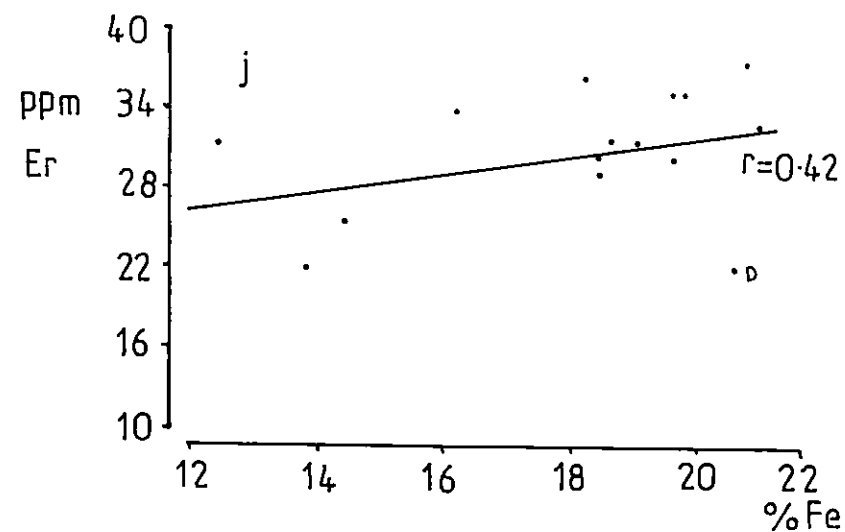
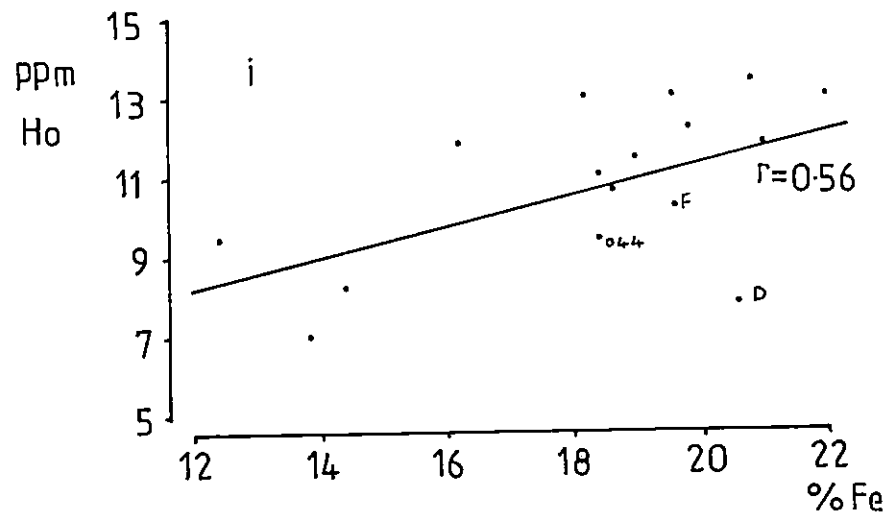


Fig. 36 (cont.)

controlled by a phase other than Fe. Furthermore, the coefficients of variation of the heavy REE are lower than those of the light and intermediate REE, inferring less variable abundances in the crusts' major phases.

The above discussion suggests that whilst the geochemistry of the light and intermediate 3+ REE is controlled dominantly by the Fe phase, the geochemistry of the heavy REE is controlled by both the Mn and Fe phases.

As found by previous workers (Goldberg et al. 1963, Piper 1974b, Elderfield et al. 1981a) Ce behaves anomalously with respect to the 3+ REE. The geochemistry of Ce is treated more fully in section 5.8.

Three crusts exhibit anomalous REE concentrations. Compared to its Fe content, O44 is depleted in light-intermediate REE but contains 'normal' concentrations of heavy REE. In this respect its REE geochemistry is much closer to that of O41, O45 6/13A and O58 2/2B, which have lower Fe contents and higher Mn/Fe ratios.

Samples O62 1/3D and O62 1/3F, which exhibit peculiar transition element geochemistry (section 3.4) also show uncharacteristic REE geochemistry. O62 1/3D has a La content predicted by the Fe-La regression line, is enriched in Ce and increasingly depleted in heavier REE (Fig. 35). O62 1/3F is enriched in La and Ce, depleted in intermediate REE and contains predicted abundances of heavy REE. No explanation is offered for these patterns.

5.5 Rare earth element fractionation

Because average shale has similar REE contents to most marine phases, fractionation of the REE is best studied using shale-normalised data. Shale-normalised patterns of the crusts are shown in Fig. 35.

Piper (1974b) observed that deep-water (> 3000-3500 m) nodules were commonly depleted in both light and heavy REE relative to intermediate REE whereas shallow-water nodules

(< 3000 - 3500 m) were generally light and heavy REE enriched (Table 31). Elderfield et al. (1981a) found that deep-water, diagenetically influenced, todorokite-rich nodules from the NE equatorial Pacific fell correspondingly into the deep-water category, and explained the pattern in terms of the relative proportions of a P-rich phase with a REE pattern similar to that of biogenous apatite and an Fe-rich phase with a REE pattern the mirror image of that for seawater. In contrast, the REE patterns of some deep-water nodules from the SE Pacific were slightly enriched in heavy REE (Courtois and Clauer 1980), although in the absence of other chemical data interpretation is precluded.

The shale-normalised patterns of the crusts fall into two categories:-

1. Showing a marked enrichment along the intermediate REE, and no depletion of the heavy REE, very similar to the pattern of the Bauer Basin Crust (Table 31, Fig. 35).
2. Showing a less marked enrichment along the intermediate REE, and a depletion of heavy REE relative to Gd-Dy. This slightly 'convex' pattern is dissimilar to the previous categories but falls between Piper's deep-water and shallow-water patterns. (Table 31).

Only two crusts, O62/ 1/3D and O62 1/3F, do not fall into either category. O62 1/3D has a flat intermediate REE pattern and is heavy REE depleted, whilst O62 1/3F is La enriched and Dy depleted (Fig. 35).

Pattern (1) is exhibited by samples O41, O44, O45 6/13A, O58 2/2B and possibly O51 6/7A, O53 1/1D and O55 3/3. The last three are contaminated with significant quantities of phillipsite or francolite, both of which have REE patterns very different to those of ferromanganese oxides and more similar to that of seawater (Piper 1974a). It seems likely that for these samples the enrichment along the intermediate REE represents a phillipsite or francolite REE signature superimposed upon a ferromanganese oxide REE signature. These samples

Table 31 Rare earth element enrichment ratios and Ce anomalies in marine ferromanganese deposits

	Light REE enrichment La/Sm	Heavy REE enrichment Yb/Sm	Dy/Nd	Ce anomaly
Mean crusts	1.11(+0.22)	1.28(+0.44)	1.47(+0.21)	+0.53(+0.19)
Crusts < 2000 m	1.30(+0.24)	1.81(+0.53)	1.68(+0.17)	+0.58(+0.15)
Crusts > 2000 m	1.03(+0.18)	1.01(+0.13)	1.34(+0.13)	+0.59(+0.12)
Shallow water nodules (<3000 m) ^a	1.18(+0.21)	1.41(+0.44)		+0.22(+0.16)
Deep water nodules (>3000 m) ^a	0.79(+0.18)	0.78(+0.18)		+0.18(+0.15)
NE Equatorial Pacific nodules ^a	0.54(+0.03)	0.94(+0.06)	1.45(+0.08)	+0.20(+0.13)
Bauer Basin nodules ^a	0.95(+0.03)	1.69(+0.08)	1.78(+0.10)	-0.23(+0.06)
Bauer Basin crust ^b	1.11(+0.03)	1.69(+0.08)	1.78	-0.23(+0.06)
Bauer Basin crust ^b	1.11	1.66		-0.28
EPR crest sediment ^b	1.07	2.41		-0.83
Seawater ^b	1.11	3.03		-0.42

^a Data from Piper (1974b)

^b Data from Elderfield + Greaves (1981, 1982)

$$\text{Ce anomaly} = \log \left(\frac{\text{Ce}}{\frac{2}{3}\text{La} + \frac{1}{3}\text{Nd}} \right)$$

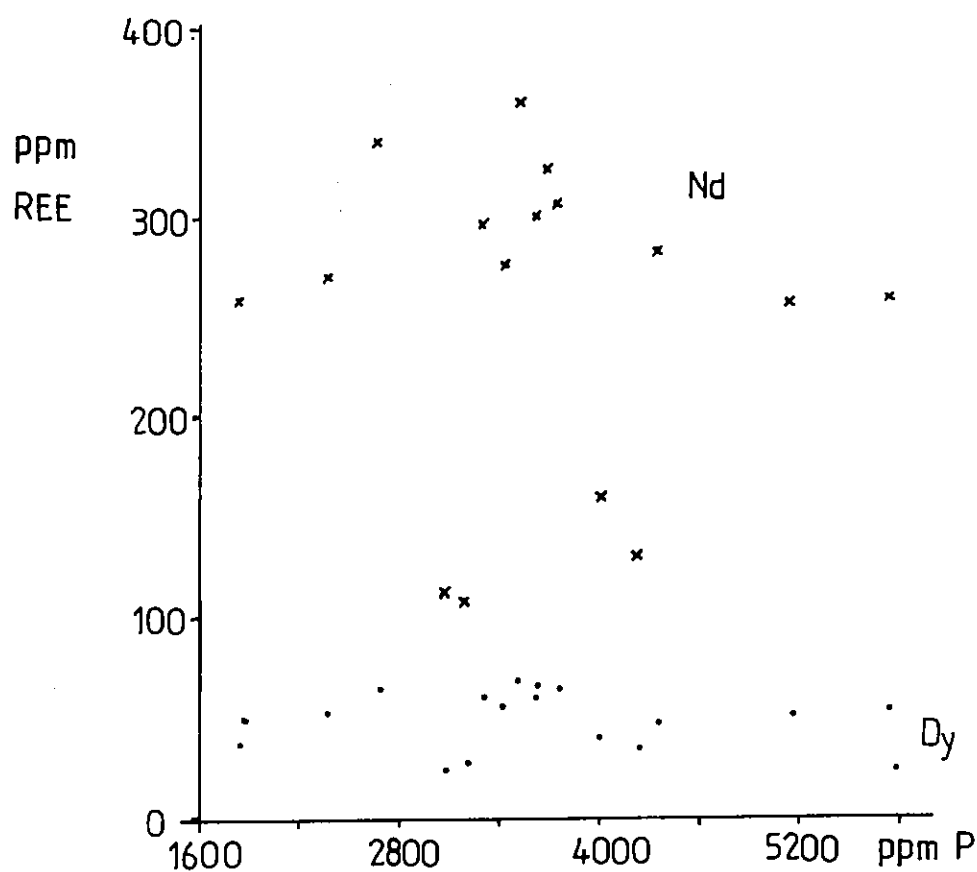


Fig. 37 Scatter plot of phosphorous versus Nd(x) and Dy(.) in the LI crusts.

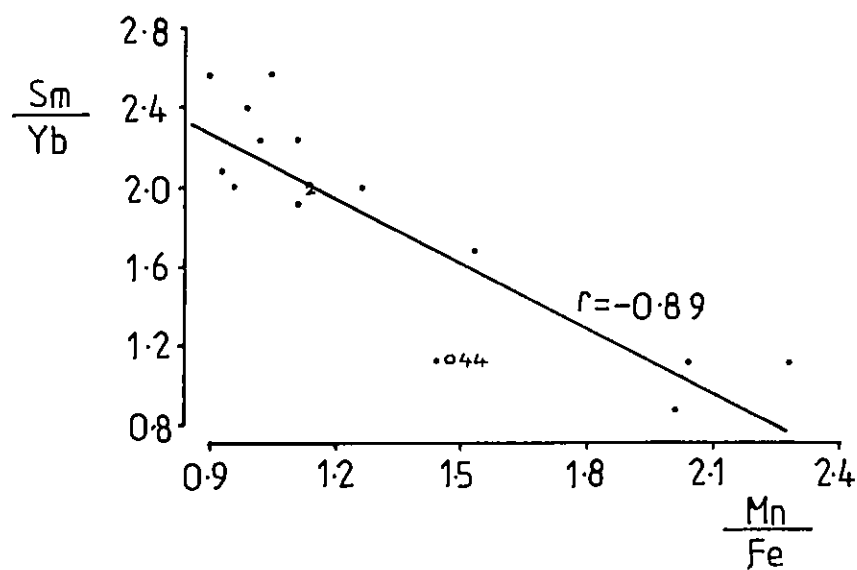


Fig. 38 Plot of Sm/Yb vs. Mn/Fe, indicating the fractionation of intermediate REE from heavy REE with increasing Mn/Fe ratio.

will not be discussed further.

Other crusts showing this pattern are those from shoaler than 2 km with high Mn/Fe ratios and transition element geochemistry correspondingly different from crusts from below 2 km (Sections 4.4.3, 4.6). It is proposed here that the same process that increases the Mn/Fe ratios of crusts and affects the transition element geochemistry - i.e. a greater concentration of dissolved Mn associated with the O_2 minimum between 1 + 2 km depths leading to increased adsorption onto and occlusion of both Mn and Fe oxyhydroxide flocs - also controls the REE abundances and patterns in the crusts.

The discussion on the incorporation of REE into the crusts showed that whilst the light and intermediate REE were accumulating mainly with the Fe-phase, the heavy REE accumulated with both the Fe and Mn phases. Thus processes affecting the Mn/Fe ratio will also affect the relative accumulation of the REE. As the Mn/Fe ratio increases, the intermediate REE become increasingly fractionated from the heavy REE (Fig. 38). Furthermore, the regression lines of intermediate REE versus Fe (Fig. 36 c-h) yield negative intercepts on the y axis.

This may be explained either by assuming that a certain amount of Fe, equal to $\left| \frac{\text{intercept}}{\text{slope}} \right| \%$, is contained in a phase which has no association with REE, or by a ratio of REE/Fe which increases with Fe. This may be the case for the intermediate REE (Fig. 39a), but not for the heavy REE (Fig. 39b).

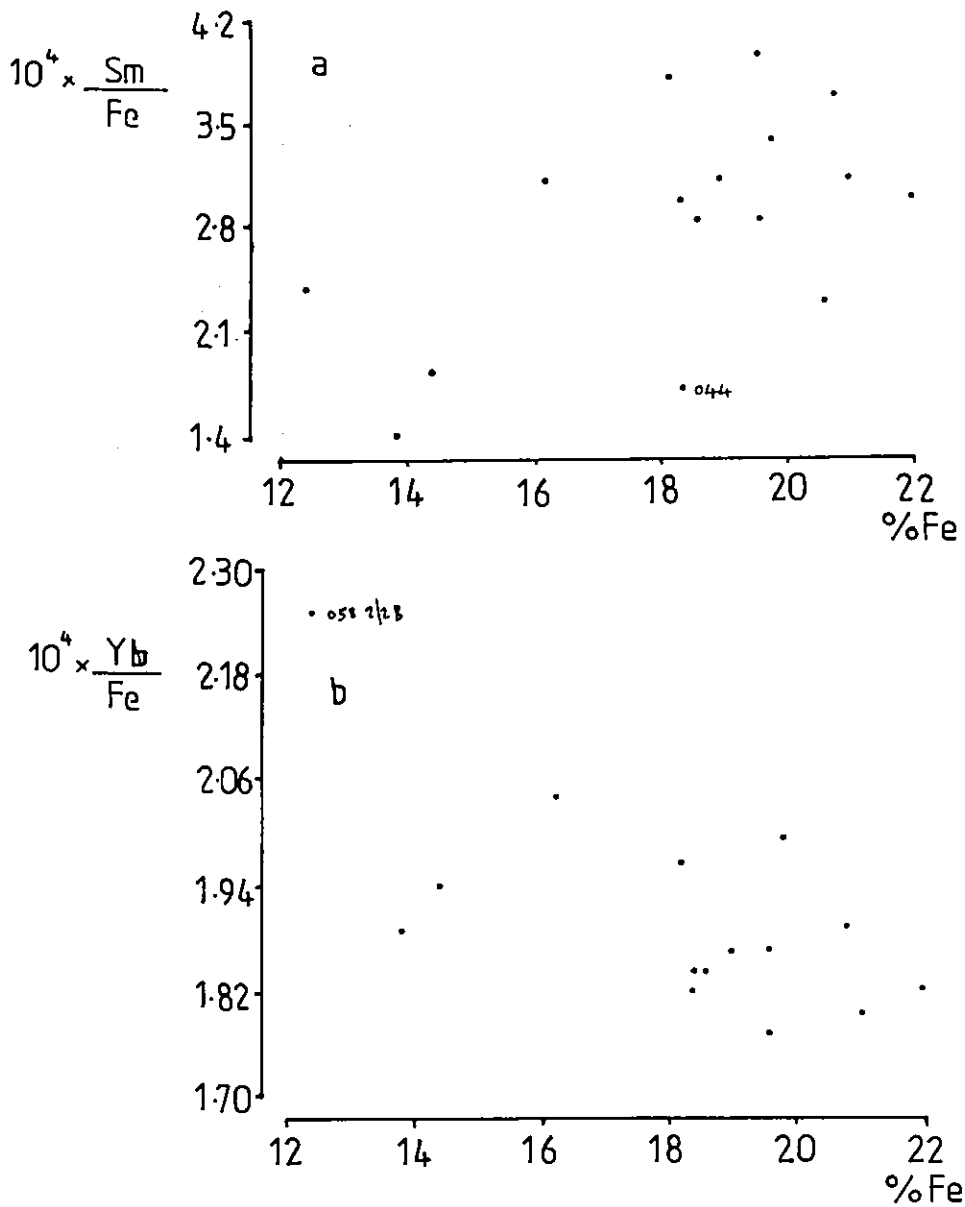
The same relation is seen for regression lines between strongly Mn-associated elements - Co, Mo, Pb - and Mn. (Section 4.6.4). Thus, at depths at which a higher dissolved Mn content leads to a greater occlusion of Fe oxyhydroxide flocs, crusts exhibit enhanced concentrations of elements more specifically adsorbed by Mn oxyhydroxide, and decreased concentrations of elements more specifically adsorbed by Fe oxyhydroxide.

Two crusts, O44 and O58 1/2, do not adhere precisely to the above. O44, which has a Mn/Fe ratio similar to that of O50 4/6A + O63 2/9A, has a REE geochemistry and a transition element geochemistry much closer to that of crusts with higher Mn/Fe ratios. (Fig. 38). Its occurrence at 1,950 m, compared with 4325 m for O50 4/6A and 2325 m for O63 2/9A, suggests that occlusion by Mn adsorption has played an important role in its development. The converse is true for O58 1/2, which was dredged at 1,250 m but has a deep water REE pattern and a deep water transition element chemistry; this is surprising in view of the shallow-water geochemistry of O58 2/2, from the same dredge haul. No explanation can be given for this; however, Craig et al.'s (1982) results for a suite of crusts dredged from 0.8 - 2 km on the Hawaiian Archipelago show that whilst the Mn/Fe ratio is, on average, high in this depth range, it is not universally high, implying that the dissolved Mn content of seawater varies on a horizontal scale.

5.6 Comparison with Bauer Basin crust

Whilst the absolute abundances of the 3+ REE from the Bauer Basin (>4000m) ferromanganese crust reported by Elderfield and Greaves (1981) are depleted on average 2-3 times compared to the Line Islands crusts, their relative abundances are similar to LI crusts with high Mn/Fe ratios (Table 31, Fig. 35). The Bauer crust, in comparison, has a Mn/Fe ratio of 0.82. A LI crust of similar Mn/Fe would be expected to be much less enriched in, or depleted in heavy REE, relative to Sm (Table 31). However, the apparent anomaly is in fact in keeping with the mechanisms suggested for the LI crusts.

Much of the Fe and Mn collecting in the Bauer Basin is considered to be derived from hydrothermal activity on the adjacent East Pacific Rise (Dymond and Veek 1975, Heath and Dymond 1977). On meeting ocean bottom water, Fe^{2+} in hydrothermal solutions rapidly oxidises and



Figs. 39a,b Plots showing the variation in the REE/Fe ratio with Fe content of the LI crusts, for (a) intermediate REE and (b) heavy REE.

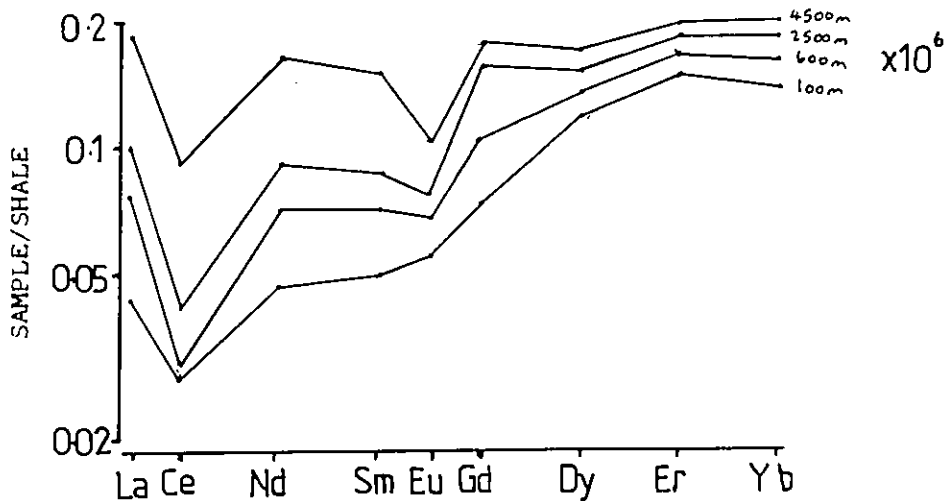


Fig. 40 Shale normalised REE patterns for seawater. Data from Elderfield and Greaves (1982).

precipitates as Fe oxyhydroxide, whilst the same reaction is more sluggish for Mn^{2+} (Stumm and Morgan 1970), yielding high dissolved Mn^{2+} concentrations in the bottom water. (Klinkhammer et al, 1977). The same process of adsorption of Mn and subsequent occlusion of Fe oxyhydroxide is envisaged as proposed for the 1-2 km LI crusts. In the absence of the adsorbed Mn, one would expect a REE pattern dominated by the Fe-phase akin to those for the deeper water crusts. The same may be said of EPR crest sediment, although in this case there is the complicating factor of the presence of foraminiferal calcite, which, like seawater, is strongly heavy REE enriched (Elderfield et al. 1981a, Table 3.1).

5.7 Comparison with seawater

Since Piper (1974b) has concluded that the REE contents of deep-water nodules are responsible for the REE pattern of seawater, whilst Bender et al. (1971) and Piper and Graef (1974) have concluded that the REE pattern of EPR crest sediments reflects that of seawater, a comparison of the seawater pattern with those of the LI crusts is worthwhile.

The only systematic study of the REE distribution through the water column has been made by Elderfield and Greaves (1982) for a station in the N.E. Atlantic. Their results are shown in Fig. 40. Excepting the section of the water column which comprises Mediterranean outflow water, the changing distribution is explained in terms of boundary layer inputs, removal by biogenic and inorganic particles in the mixed layer and dominant regeneration in deeper water. Because the profiles of the light REE resembles that of Cu, and the dissolved Cu profile has been found to be similar in both Pacific (Boyle et al. 1977) and Atlantic (Moore 1978) water columns, the REE distribution in the Pacific water column may be expected to be similar to that in the Atlantic. Comparison of the Pacific crusts with the Atlantic water is therefore valid.

Whilst the trend of declining REE enrichment with increasing depth noted by Elderfield and Greaves (1982) is reflected by the shallow-deep crust patterns, in detail the patterns show distinct differences indicating that the crusts neither reflect nor are responsible for the seawater pattern. Firstly, no Eu anomaly is seen in any crust. Secondly, many crusts are depleted in heavy REE (relative to intermediates) whereas all seawater samples are heavy REE enriched. Thirdly, a far greater change in the seawater pattern occurs between 2,500 m and 4,500 m than between 600 m and 2500 m (Fig. 40), whilst in depth terms the two patterns noted for crusts occur above and below 2,000 m.

5.8 Geochemistry of Ce

Studies on the REE geochemistry of ferromanganese nodules and of seawater (e.g. Goldberg et al. 1963, Piper 1974b, Elderfield et al. 1981a, Elderfield and Greaves 1982) have shown that Ce exhibits a fundamentally different behaviour to the 3+ REE in the marine environment. Goldberg (1961) has attributed this to its oxidation from the soluble trivalent state to the less soluble tetravalent state and its removal from seawater into authigenic phases. This is supported by the observation that whereas the shale normalized contents of seawater show a marked depletion in Ce compared to its neighbours La and Pr or Nd (yielding a negative Ce anomaly), most oceanic ferromanganese deposits show a strong enrichment in Ce (positive Ce anomaly) (e.g. Piper 1974b, Addy 1979).

5.8.1 Ce contents

The Ce contents of the crusts average 972 ppm, more than double that of N. Pacific todorokite-rich nodules, similar to that of SMnO_2 -rich nodules described by Piper (1974b) (890 ppm, Table 28) and less than that reported by Addy (1979) for SMnO_2 -rich Atlantic nodules (2057 ppm). The enhanced Ce content of the SMnO_2 -rich hydrogenous crusts supports Elderfield et al.'s (1981a, b) proposal

that Ce is added to nodules directly from the water column and that nodules with the greatest seawater influence have the greatest Ce contents.

The correlation matrix (Table 30) indicates that unlike its neighbours La and Pr, Ce shows no strong relation with Fe, and is negatively correlated with Mn. The high Ce contents of some crusts with high Mn/Fe ratios (Table 27), however, suggests that Ce may be removed from the water column by both Fe and Mn oxyhydroxides.

5.8.2 Ce anomalies

Because Ce is removed from seawater in the 4+ valency state it has been suggested that the magnitude of the Ce anomaly may be a function of the redox potential of the depositional environment (Glasby 1973, Piper 1974b, Addy 1979). Despite the difficulties involved in measuring Eh in the marine environment (e.g. Ruppert 1980) the wide range of both positive and negative Ce anomalies noted in ferromanganese crusts alone mitigates against this (Morten et al., 1980, Elderfield and Greaves 1981, this study). The development of the negative Ce anomaly within the upper 500 m of the water column suggests that Ce^{3+} oxidation is possible at that depth range; furthermore, some of the largest Ce anomalies noted in this study occur in crusts dredged from within the presumed O_2 minimum. It seems likely, therefore, that Ce^{3+} oxidation can occur throughout the water column.

Elderfield et al.'s (1981a) work on NE equatorial Pacific nodules suggested that Ce was added to nodules directly from seawater. Thus nodules subjected to the greatest diagenetic influence exhibited the smallest Ce anomalies. In support of this, the upper surfaces of nodules were found to have greater Ce anomalies than the lower surfaces (Elderfield et al. 1981b). A similar process was envisaged to explain the reduced Ce anomalies in Bauer Basin nodules (Elderfield and Greaves 1981); in this case, however, negative Ce anomalies were found, which were accounted for by an input of hydrothermal Fe

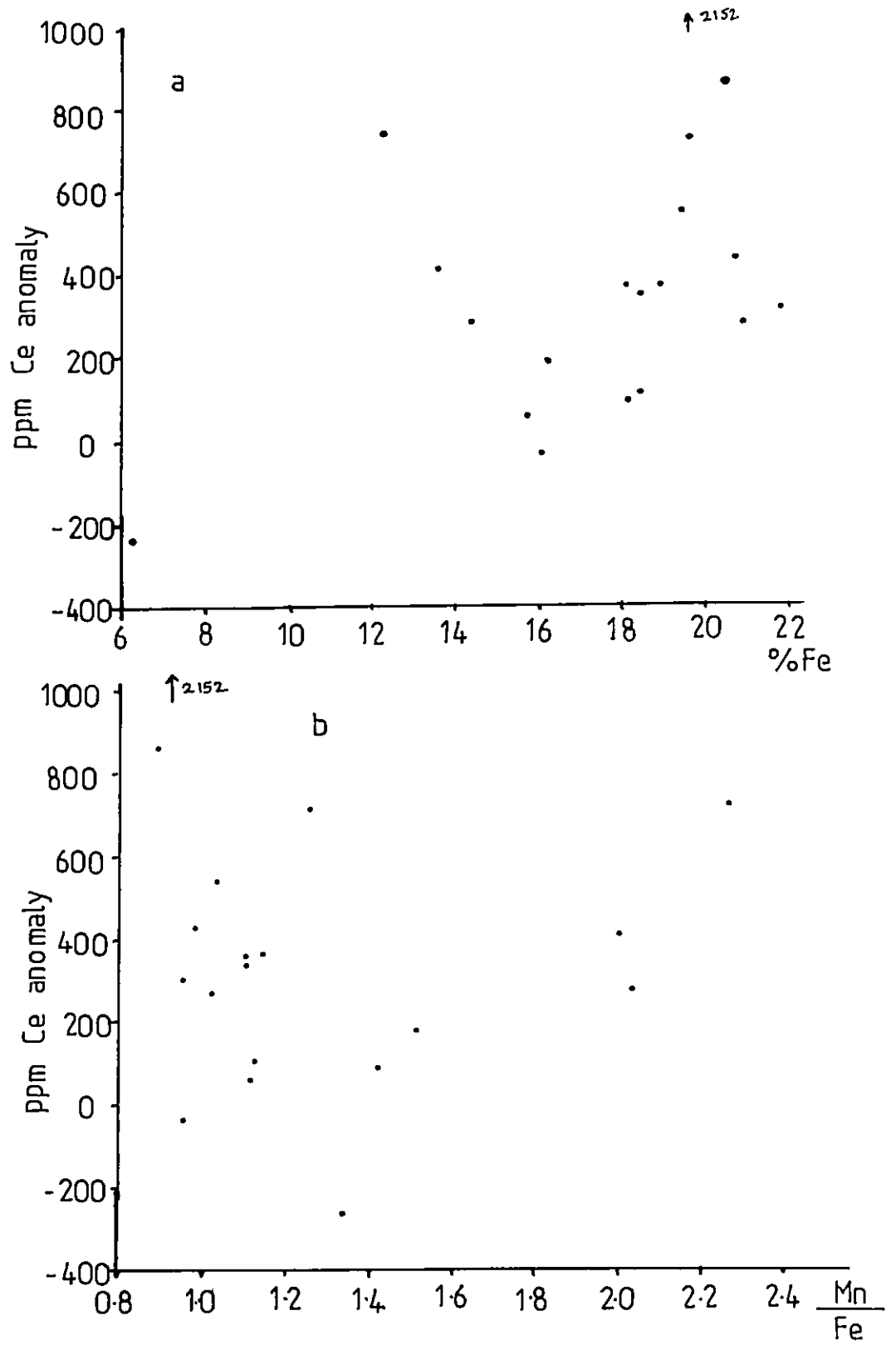


Fig.41 Ce anomaly versus (a) Fe and (b) Mn/Fe ratio of the LI crusts.

oxyhydroxide and associated REE. Elderfield's data suggests that two processes may reduce the magnitude of the Ce anomaly in ferromanganese deposits - early diagenetic reactions in associated sediment, and hydrothermal inputs. However, neither process is tenable for the LI crusts.

Because La and Nd covary much more closely with Fe than does Ce, one may expect greater Ce anomalies in crusts with low Fe contents and/or high Mn/Fe ratios. Figs. 41a + 41b indicate that this is not the case, however.

Except for crusts which are contaminated with phillipsite or francolite, which themselves have negative Ce anomalies (051 6/7A, 053 1/1D, 055 3/3), there is no obvious control on the Ce anomaly. One speculative possibility is that the Ce anomaly is a function of the time-span between the precipitation of a Mn/Fe oxyhydroxide floc in the water column and its accumulation as a ferromanganese deposit. In support of this, Elderfield and Greaves (1982) have pointed out that whilst surface removal processes for the 3+ REE are restricted to the mixed layer (100 m), the characteristic negative Ce anomaly develops over the upper 500 m suggesting a further removal of Ce over a greater period of time.

It is interesting to note that the LI crusts are much more enriched in Ce compared to the 3+ REE than the Bauer Basin crust, which is itself enriched in Ce over any 3+ REE relative to seawater. The oxides in the Bauer Basin crust are derived predominantly from hydrothermalism on the East Pacific Rise (Lyle 1981). If we may make the assumption that these oxides reside in the water column for a relatively short time prior to accumulation in the crusts, then we may speculate that the removal of Ce from the water column may be no less rapid than that of the 3+ REE, but may be more complete.

5.8.3 Comparison with Ti, Pb and Co

Because Ce, Ti, Pb + Co are elements which are removed from seawater in the higher valence state (Ce^{4+} ,

Ti⁴⁺, Pb⁴⁺, Co³⁺, Goldberg 1961) it may be envisaged that processes resulting in Ce enrichment may also result in the enrichment of Ti, Pb and Co. However, no relation is seen between Ce, Ti and Pb in the crusts, and a weak negative correlation exists between Ce and Co (Fig. 42). This is in contrast to diagenetically influenced nodules which show a strong positive Ce-Co correlation (Elderfield et al. 1981a).

The dissimilar behaviour of Ce, Co, Ti + Pb in the crusts is strong evidence that their geochemistry is not well explained in terms of a varying redox potential. Rather, examination of the correlation matrices (Tables 6 + 30) suggests that the main control is the affinity of each for the Mn and Fe phases. Particularly, the weak negative correlation between Ce and Co is a function of the strong affinity of Co to Mn, and the weaker affinity of Ce to Fe.

The covariation of Ce and Co noted by Elderfield et al. (1981a) in diagenetically influenced nodules may be explained by the accumulation of both elements directly from the water column and their non-involvement in early diagenetic reactions. The paradox that Co is adsorbed by Mn oxyhydroxide and is associated with δMnO_2 in ferromanganese crusts (Craig et al. 1982, Friedrich and Schmitz-Wiechowski 1980, this study) whilst covarying with Fe in diagenetically influenced nodules (Elderfield et al. 1981a; also Goldberg 1954, Willis and Ahrens 1962, Burns and Fuestenau 1966) is resolved by considering the authigenic phase of nodules as a two component system comprising a diagenetic phase and a seawater phase. The former comprises mainly todorokite and is rich in Mn, Cu, Ni + Zn; the latter comprises δMnO_2 and amorphous $\text{FeOOH}\cdot\text{H}_2\text{O}$ and has a similar composition to deep water ferromanganese crusts. Overall, a positive Fe-Co correlation is seen; within the seawater phase, however, the Co is associated with the Mn which itself is closely associated with Fe oxyhydroxides. (Burns 1976).

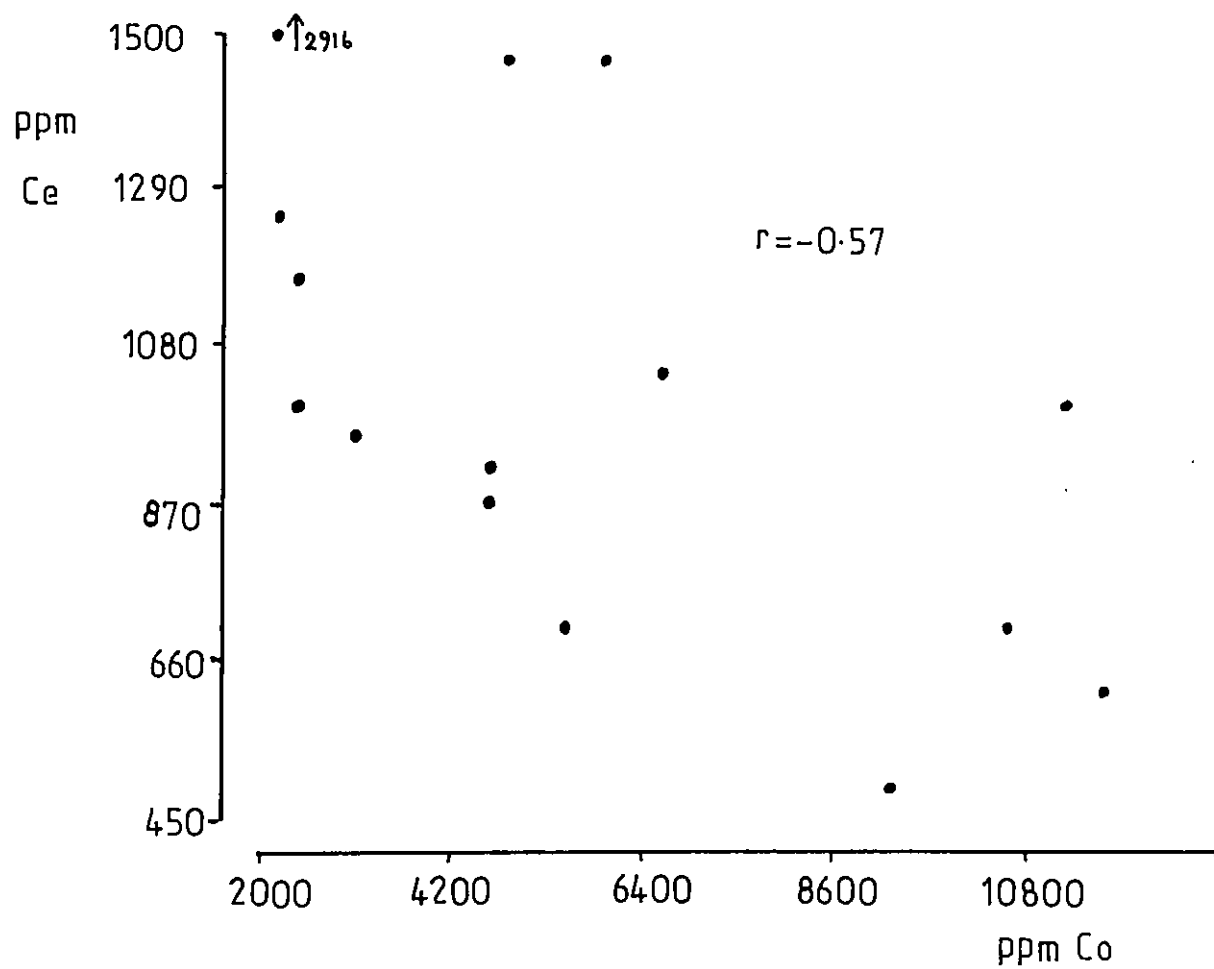


Fig.42 Plot of Ce versus Co in the LI crusts.

SECTION 2

Ferromanganese nodules and associated sediments from
the S.W. equatorial Pacific.

CHAPTER 6 INTRODUCTION

The pioneering work of Mero (1962, 1965) on the regional variations in the chemical composition of Fe-Mn nodules from the Pacific Ocean suggested that the most prospective region for ore-grade nodules was the N.E. equatorial zone. As a consequence much research was concentrated in that area, to the detriment of other Pacific regions. Thus prior to 1975 little was known concerning the distribution and chemistry of S.W. Pacific nodules. Both Price and Calvert (1970) and Skornyakova and Andrushchenko (1974) had published general maps of elemental variations in nodules from throughout the Pacific. On the basis of very few samples, both delineated the S.W. Pacific as a nodule province of low Mn/Fe ratio with low Ni and Cu contents. Interestingly, more recent work has largely confirmed those initial considerations (Piper and Williamson 1977, Glasby et al. 1981). In 1974 Glasby and Lawrence (1974 a-g) published a series of maps elucidating the distribution and chemistry of nodule deposits in the S. Pacific.

The setting up of the Committee for Co-ordination of Joint Prospecting for Mineral Resources in South Pacific Offshore Areas (CCOP/SOPAC) in 1972 accelerated the exploration for nodules in the S.W. Pacific. The results of 17 CCOP/SOPAC cruises to the region between 1974 and 1981, 2 New Zealand Oceanographic Institute cruises to the S.W. Pacific Basin and Samoan Basin (Meylan et al. 1975, Glasby et al. 1975, 1981, Meylan et al. 1978) and one ORSTOM (Noumea) cruise to the South Penrhyn Basin have been summarised by Glasby (1976) and more recently by Exon (1981, 1982, in press). Furthermore a series of cruises to the Central Pacific Basin by the Japanese Geological Survey (Mizuno and Chujo 1975, Mizuno and Moritani 1977, Moritani 1979, Mizuno 1981, Moritani and Nakao 1981) and to the Tuamotu - Marquesas region by the CNEXO (Pautot and Hoffert 1974, Pautot and Melguen 1976, 1979) extended our knowledge of nodule deposits in adjacent areas.

Exon (1981, in press) has used all the available data from the CCOP/SOPAC, NZOI, ORSTOM and Japanese cruises (and including the analyses of this work), in addition to information from the Scripps Data Bank to examine variations in nodule grade and abundance in and around the present study area (Fig. 43). His principal conclusions may be summarised as follows:-

1. Nodules are concentrated between 4,500 m and 5,500 m, a finding in agreement with that of Pautot and Melguen (1976, 1979), who suggested that nodules in the Tuamotu - Marquesas region were most abundant at depths between the lysocline and the CCD.
2. Major variations in nodule abundances and grades fall into 3 latitudinal zones -
 - a. a southern zone, 9-25°S, including the South Penrhyn, Samoan and S.W. Pacific Basins, containing low grade nodules in high concentrations,
 - b. a central zone, 5-9°S, in the North Penrhyn Basin, containing nodules of moderate grade in low concentrations,
 - c. a northern zone, 5°S - 6°N, confined to the East Central Pacific Basin and containing nodules of variable but often high grade in moderate to high concentrations. Nodules of low grade in low abundance are found in the 1°N - 1°S zone, where carbonate sedimentation rates are at a maximum.

Exon explains the regional trend of higher nodule grades towards the equator in terms of a greater biogenic input of metals, the model proposed to explain the high metal contents of N.E. Equatorial nodules (Greenslate et. al. 1973). The importance of the lysocline and the CCD is thus stressed, since it is assumed that the greatest skeletal dissolution and metal release occurs at that depth range.

Glasby (1981) has pointed out that the sedimentation rate is an important factor in controlling nodule abundance in the region. High nodule densities ($>20 \text{ kgm}^{-2}$) are found in the S.W. Pacific and S. Penrhyn Basins where

biological productivity is low and there is little input of terrigenous or volcanoclastic material. Abundances in the S.W. Pacific Basin decline towards New Zealand (Meylan et al. 1975) and in the Samoan Basin decline westwards, where volcanoclastic input from the Tonga-Kermadec volcanic arc is greatest (Meylan et al. 1978).

Topographically constrained and accelerated bottom currents inhibit sedimentation or actively erode sediment, yielding conditions favourable for nodule formation. This is well documented in the Samoan Passage (Hollister et al. 1974). Scour marks on precision depth records from the Aitutaki Passage (Landmesser et al. 1976) and from the Marquesas Fracture Zone (Pautot and Melguen 1979) suggest the same phenomenon is occurring in those areas.

The little mineralogical work performed on nodules in the region (Meylan 1976, Glasby 1978) suggests that SMnO_2 is the dominant Mn oxide mineral, with todorokite occurring rarely.

Nodule research in the S.W. Pacific is still in its descriptive stage. Almost no work has been performed concerning the genesis of the deposits or the nodule - sediment relationships. The present work aims to bridge that gap.

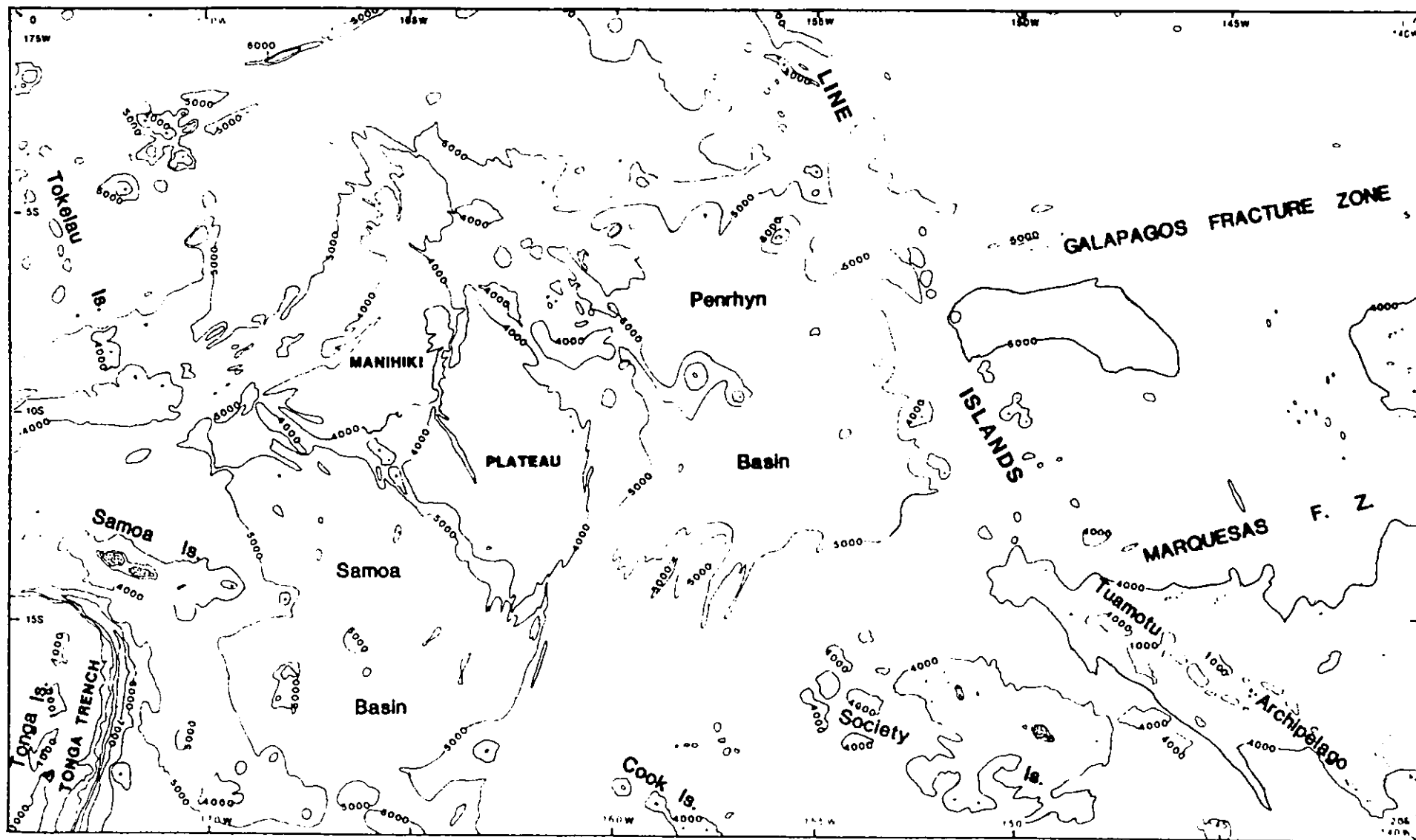


Fig.43 Bathymetry of the S.W.equatorial Pacific Ocean. (after Mammerickx et al. 1971,1973)

Chapter 7 Regional Geology

7.1 Tectonic Structure

The west central Pacific Ocean is a region of complex topography, consisting of Cretaceous oceanic crust upon which subsequent volcanism has formed upstanding tectonic elements. These are the Manihiki Plateau, and the Line Islands, Tuamotu, Tokelau, Samoan, Society Islands and Cook Islands Archipelagos, which divide the deeper areas into the Penrhyn, Tokelau, Samoan and Northeast Pacific Basins (Fig. 43). The last mentioned is situated to the east of the LIA.

The bathymetry of the region is rather poorly known, but has been mapped in a general way by Mammerickx et al. (1971, 1973). Throughout, there is a general westwards deepening of the basin areas. Thus to the east of the LI, water depths are typically 4.8 - 5.1 km, increasing to 5.2 - 5.5 km in the Penrhyn Basin with broad areas deeper than 5.5 km in both the Tokelau and Samoan Basins. Basins are interconnected by deep regions or passages:- the Penrhyn and Samoan Basins by the Aitutaki Passage, (Pautot and Melguen 1979); the Samoan and Tokelau Basins by the Samoan Passage (Hollister et al. 1974); the Penrhyn and N.E. Pacific Basin by the wide deep areas between islands of the LIA.

The bathymetry of the Penrhyn Basin has been briefly described by Winterer et al. (1974) and Exon (in press). Most obviously, the western part exhibits a more dissected topography than the eastern sector, associated with the transition from the 5.3 km deep basin to the Manihiki Plateau at 2.5 km. The transition zone is 100 km wide; within which topography is extremely rough, yielding sediment-free ridges alternating with depressions containing depth-related sediments (Bezrukov 1972). Further, an east-west trending rise, including both Tongareva and Starbuck Islands, occurs at around 10°S.

7.2 Tectonic History

The complex topography of the region, allied to the fact that important aspects of its tectonic history occurred during the late Cretaceous magnetically quiet period (110 - 85 My) has led to much speculation concerning the evolution of the Central Pacific (e.g. Malahoff 1971, Larson and Chase 1972, Winterer 1973, 1976, Larson 1976, Jackson and Schlanger 1976, Orwig and Kroenke 1980).

The occurrence of the Mesozoic - Phoenix magnetic lineations (M-series of Larson et al. 1972) in the western Central Pacific Basin, of which the youngest is timed at 108 My (at 2°S , 180°), and the observation of anomaly 32 (76 My) in crust 400 km SE of the Nova Canton trough, (i.e. at 5°S 165°W), suggests that the evolution of the region was complicated by ridge crest jumping and changes in ridge orientation. Larson and Chase (1972) have suggested that the triple point of the Pacific, Farallon and Phoenix plates migrated rapidly 400 km southwards from the Nova-Canton trough between 108 My and 76 My. At approximately 105 My, it is considered (Winterer et al. 1974) that the triple point occupied a position on or close to the Manihiki Plateau. The excessively thick crust of tholeiitic basalts is suggested to be due to the position of the triple point above a major melting spot in the mantle; triple points are thought to frequently occur in such positions (e.g. the Magellan and Shatsky Rises, Larson et al. 1972).

The tectonic setting and evolution of the LIA has been discussed in Chapter 1. Briefly, the archipelago represents a double linear chain of atolls, guyots and seamounts stretching SE a distance of 3,500 km from Horizon Guyot (19°N 169°W) and the Tuamotu Archipelago at 15°S . South of the equator, positive features are rather scarce, and are separated by basinal areas deeper than 5,000 m (Fig. 43).

Age dating of late stage volcanic rocks and of shallow water reefal faunas along the archipelago (Winterer, Ewing et al. 1973, DSDP Scientific Staff 1974, Saito and Ozima

1976, Beckmann 1976) suggests that the majority of volcanic activity occurred throughout the archipelago between 70 and 85 My, although sporadic volcanism continued into the Eocene (Saito and Ozima 1976, Haggerty et al. 1982). Petrological work (Natland 1976) shows that the volcanism is of an oceanic island type, i.e. characteristic of mid-plate volcanism. Orwig and Kroenke (1980) have suggested that the archipelago may represent the position of a large transform fault separating the East Pacific Rise from an active spreading ridge south of the mid-Pacific mountains. Volcanism, which was widespread in the Central Pacific during the Late Cretaceous (Schlanger et al. 1981), may be expected to have been concentrated along such crustal weaknesses.

Wilson (1963b) has summarised the sparse geological information concerning the Cook, Tuamotu, Phoenix and Tokelau island groups. The southern Cook Islands, which abut onto the study area, are of Lower Tertiary or Cretaceous age, whilst Mahatea, in the N.W. of the Tuamotu group, has limestones of probable Eocene age.

More recent volcanism has occurred in the Samoan and Society Islands Archipelagos and in the Tongan volcanic arc. Lonsdale (1975) and Natland (1980) have pointed out that the six Samoan islands were built dominantly during the Pliocene and comprise mainly olivine basalts. Volcanism has continued sporadically into Recent times. In the Society Islands, Wilson (1963b) has documented Recent volcanic activity on Mehetia, whilst Dymond (1975) has dated Tahitian lavas at 2 My.

7.3 Sedimentation

The sediment isopach map drawn by Ewing et al. (1969) from seismic profiles indicates that away from island chains total sediment thicknesses are generally less than 100 m, rising to a maximum of 200 - 300 m in the higher productivity equatorial region in the east of the study area.

Sediment piles are much thicker on the plateaus and on the archipelagic aprons (Lonsdale 1975). Up to 1 km of carbonate sediments occur both on the Manihiki Plateau and in the troughs which cut it. Sediment types associated with the island chains include fine-grained volcanoclastic or calcareous turbidites, and coarse-grained breccias and conglomerates which are deposited as debris flows on the steep slopes of guyots and seamounts (Cook et al. 1976).

Deep water turbidites, derived from the LIA and the Central Basin Rise, occur throughout the eastern Central Pacific Basin (Lineberger 1975, Orwig 1981). Whilst not documented in the Penrhyn Basin, it seems likely that turbidites will occur, although to a lesser extent, in the east of the basin, and adjacent to the Manihiki Plateau.

Where topographically constrained, the flow of Pacific Bottom Water may become sufficiently intense to inhibit sedimentation or to cause erosion. Current-controlled sedimentation is most clearly documented in and around the Samoan Passage (Hollister et al. 1974, Lonsdale 1981); since the late Oligocene deceleration of Pacific Bottom Water as it leaves the passage has deposited patches of reworked sediment on Paleogene clay and on a scoured Mesozoic terrain. Scour marks have also been identified on precision depth records in the Aitutaki Passage (Landmesser et al. 1976) and in the Marquesas Fracture Zone (Pautot & Melguen 1979), charting the course of Pacific Bottom Water.

Chapter 8 Oceanography

8.1 Introduction

Manganese nodules are scarce or absent in regions of high sedimentation rates such as continental margins and the equatorial zone of carbonate-rich sediments. Mizuno and Moritani (1976) and Mizuno et al. (1980) have suggested that there is a general inverse correlation between nodule abundance and the mean sedimentation rate since the mid-late Tertiary, and several workers have sought a relationship between nodule chemistry and sedimentation rate (Price and Calvert 1970, Piper and Williamson 1977, Calvert et al. 1978, Elderfield et al. 1981).

Bottom currents affect rates of sedimentation and sediment distribution patterns by actively eroding sediment (Johnson and Johnson 1970, Hollister et al. 1974, Lonsdale 1981), by inhibiting sedimentation and possibly by affecting dissolution rates of skeletal carbonate (Edmond 1974). Furthermore it is suggested in this work that the chemistry of ferromanganese encrustations is related to oxygen levels in the water, which in turn are affected by the age and nature of ocean currents (e.g. Wyrski 1962).

8.2 Bottom Currents

Dynamical considerations led Stommel (1958) and Stommel and Arons (1960) to suggest that the deep thermohaline circulation of the oceans should consist of a northwards flow intensified along western boundaries with a broad, weaker return flow through the oceans' eastern sectors. Subsequent measurements have generally substantiated the theory, although recently Reid (1981) has pointed out the importance of mid-depth zonal flow in the Pacific away from the western boundary.

A deep western boundary current has been identified in the Tonga - Kermadec trench in the south Pacific on the basis of anomalous physical properties (principally dissolved oxygen and potential temperature, Wooster and Volkmann 1960, Knauss 1962) and by direct measurements (Reid et al. 1968, Reid 1969) (Fig. 44). This water mass, known as Pacific Bottom Water (PBW), forms by mixing, cooling and sinking in the Weddell and Ross Seas off Antarctica. It is cold and oxygen-rich. The water mass moves north, enters the Pacific Ocean to the east of New Zealand and the Chatham Rise and continues north as a western boundary current to the east of the Tonga-Kermadec Ridge (Reid et al. 1968, Reid 1969, Warren 1973). It is separated from overlying and comparatively stagnant Pacific Deep Water (PDW) by a 'benthic front' (Craig et al. 1972). The front occurs at 2 km near the Chatham Rise and dips NE so that its northern apex lies at 3.5 km at 6°N.

The continuing northwards and eastwards flow of PBW has been inferred from anomalous physical properties (Gordon and Gerard 1970, Edmond et al. 1971, Mantyla (1975), from direct measurements (Johnson 1972a, Reid and Lonsdale 1974) and from geological considerations such as sediment distribution patterns and erosional structures (Johnson and Johnson 1970, Johnson 1972b, Hollister et al. 1974, Normark and Spiess (1976), Pautot and Melguen (1979), Lonsdale and Smith (1980), Lonsdale 1981).

From the Samoan Basin PBW diverges (Fig. 44). The majority is constrained to flow through the Samoan Passage into the Central Pacific Basin (Reid and Lonsdale 1974). Although no direct measurements have been made, the occurrence of large scale sediment waves at 5000 - 5250 m on the western boundary of the Central Pacific Basin (Lonsdale and Smith 1980) suggests that the dominant flow is along the flanks of the Marshall - Gilbert Archipelago. Furthermore Edmond et al. (1971) have noted that in the centre of the Central Pacific Basin adiabatic conditions occur below 4,800 m, indicative of low flow conditions.

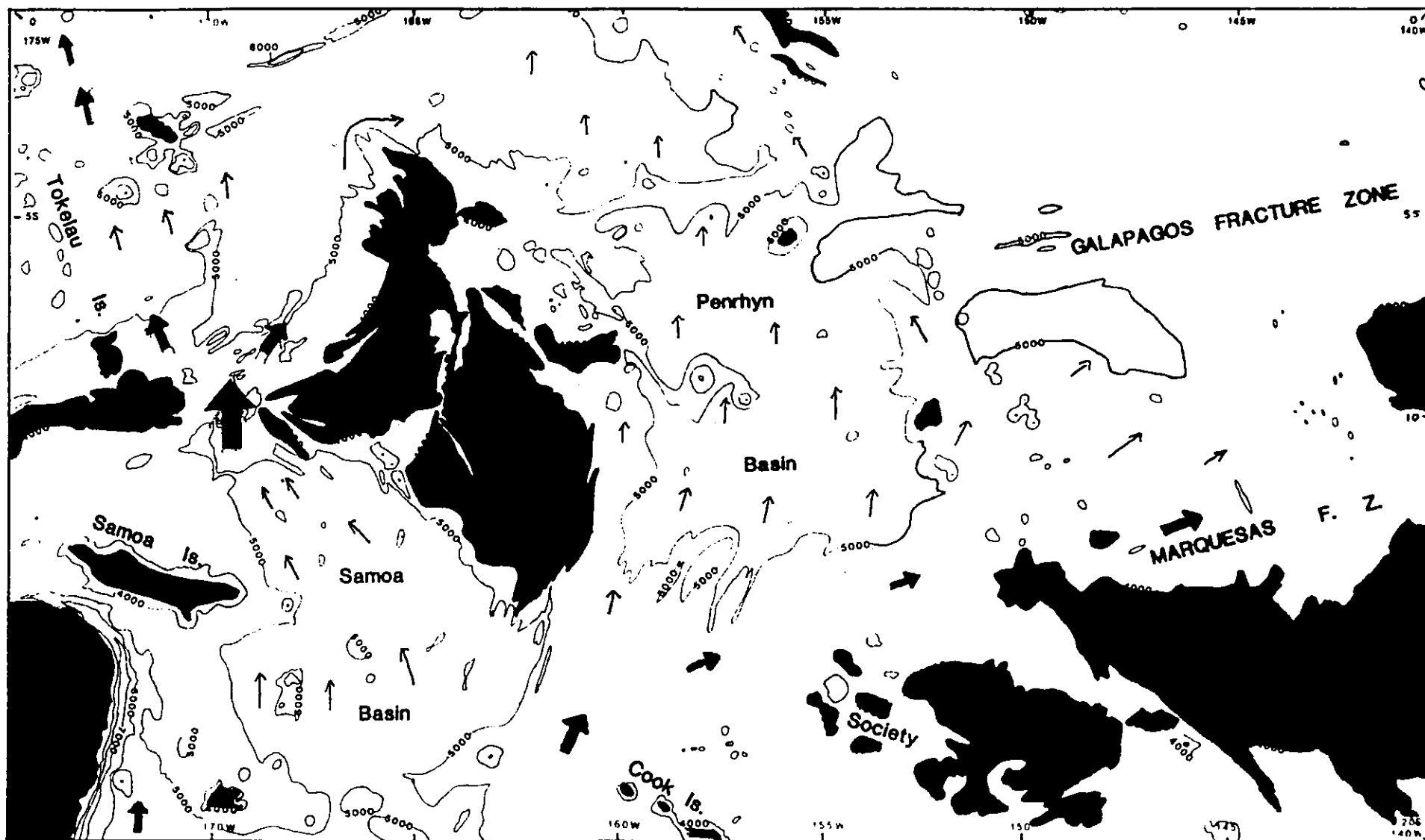


Fig.44 Flow of bottom water through the study area. Arrow size is a rough guide to current strength. Shaded areas are shallower than 4000m.

PBW flows out of the Central Pacific Basin through the Wake Island Passage (Mantyla 1975), the Horizon Passage (Edmond et al. 1971) and the Clarion Passage (Wong 1972, Mantyla 1975). Zonal flow occurs to the south of Hawaii (Edmond et al. 1971), and centred at 10°N between the Clarion and Clipperton Fracture Zones (Wong 1972).

A minority of PBW flows from the Samoan Basin to the east of the Samoan Archipelago, through the Aitutaki Passage into the Penrhyn Basin (Pautot and Melguen 1979). A broad and weak northerly flow may be envisaged through the Penrhyn Basin. Sediment distribution on abyssal hills at $3^{\circ}50'\text{S}$ $150^{\circ}45'\text{W}$, on the western flanks of the Line Islands Archipelago led Johnson and Johnson (1970) to infer a northwesterly flow along the lower flanks of the Archipelago. Normark and Spiess (1976) have invoked a flow of bottom water across the Line Islands through the Kingman Passage at 7°N to explain sediment erosion in the area.

On the basis of erosional structures and the physical characteristics of the regional bottom water, Pautot and Melguen (1979) have suggested that PBW flows east through the Marquesas Fracture Zone. This is in accordance with the observations of Wong (1972) who suggested a zonal flow at approximately 6°S . In addition, Johnson (1972a) has measured eastwards flowing currents in the Clipperton Fracture Zone.

In summary, PBW is seen to be the ubiquitous bottom water below approximately 3.5 km in the study region. It travels as a western boundary current to the Samoan Basin, from where it spreads north and north east, sluggishly in basinal areas, and more rapidly where constrained by topography.

8.2.1 Bottom Current Speeds

Throughout the region, except where constrained by topography, current speeds are very low, below 10 cms^{-1} . In the eastern Penrhyn Basin Johnson and Johnson (1970)

have measured a mean current speed of 2.4 cms^{-1} and a maximum of 5.9 cms^{-1} , and Johnson (1972a) has measured speeds of less than 10 cms^{-1} in the Clipperton Fracture Zone. In the Samoan Passage flow is topographically constrained and current speeds are greater (Reid and Lonsdale 1974, Lonsdale 1981). Upstream of the sill at the entrance to the Passage, PBW flows at $5\text{-}10 \text{ cms}^{-1}$. From the sill, where the mean flow rate is 12 cms^{-1} , the bottom water accelerates down a spillway to at least 17 cms^{-1} (Lonsdale 1981). On leaving the Passage, flow decelerates to a mean of 2 cms^{-1} , maximum $5\text{-}8 \text{ cms}^{-1}$.

Because it is likely that flow speeds in the region are at a maximum in the Samoan Passage, we can safely assume that 20 cms^{-1} represents a regional maximum velocity, with a possible mean of less than 5 cms^{-1} . The critical erosion velocity of deep ocean sediment is poorly known. On the basis of laboratory studies, however, it is generally considered to be greater than $20\text{-}30 \text{ cms}^{-1}$ (e.g. Lonsdale and Southard 1974) although sedimentation is inhibited at lower velocities. Despite this, the occurrence of hiatuses in the Tertiary and Quaternary sediment column (Moore and Heath 1977, Moore et al. 1978, Von Stackelberg 1979), of reworked sediments (Riedel and Funnel 1964, Johnson and Johnson 1970; Lonsdale 1981, Thiede 1981), of erosional structures (Johnson 1972b, Hollister et al. 1974, Kennett and Watkins 1976, Lonsdale 1980) and of current controlled depositional structures (Johnson and Johnson 1970, Johnson and Damuth 1979, Lonsdale and Smith 1980, Lonsdale 1981), all indicate that deep ocean currents have affected sediment distribution patterns in relatively recent time. In turn, this implies a more intense deep circulation in the recent past than at present, possibly during glacial periods (Johnson 1972a, Johnson et al. 1977) or during the early Cenozoic (Johnson 1974, Moore et al. 1978). At present, however, active erosion of sediment may be invoked only in those small areas such as the Samoan Passage where the flow of bottom water is topographically constrained.

8.3 Other Currents

The circulation pattern of the Pacific Ocean has been described by Sverdrup et al. (1942) and Pickard (1975), which should be referred to for more detailed information.

8.3.1 Upper Waters

The circulation in the upper waters in the Pacific (Fig. 45) consists of a clockwise gyre in the N. Pacific and a counterclockwise gyre in the S. Pacific (Pickard 1975). The N. and S. Equatorial Currents form part of the gyres and between them is the N. Equatorial Countercurrent. The S. Equatorial Current flows westwards between $8-10^{\circ}\text{S}$ and 3°N , whilst the N. Equatorial Current occurs between 8 and 20°N . Both these, plus the N. Equatorial Countercurrent, extend across almost the entire ocean.

Divergence along the boundary of the N. Equatorial Current and Countercurrent at 3°N allows nutrient-rich deeper water to penetrate into the photic zone and marks the centre of the equatorial zone of high productivity.

In addition to the three currents described above, there is a weak and narrow South Equatorial Countercurrent at $10-12^{\circ}\text{S}$ (Reid 1959) and a strong, ribbon-like eastward flowing Equatorial Undercurrent embedded within the S. Equatorial Current. It occurs between $1-5^{\circ}\text{W}$ and $1-5^{\circ}\text{S}$, between 70 and 200 m depth and extends across the whole Pacific.

8.3.2 Central Water Masses

Between about 100 m and 800 m lie the N. and S. Pacific Central Water Masses and the Pacific Equatorial Water Mass. The Equatorial Water extends across the whole Pacific, between 20°N and 10°S in the eastern Pacific, diminishing in north-south extent to the west. It is separated from the well-mixed surface layer by a strong thermocline which inhibits the transfer of water properties.

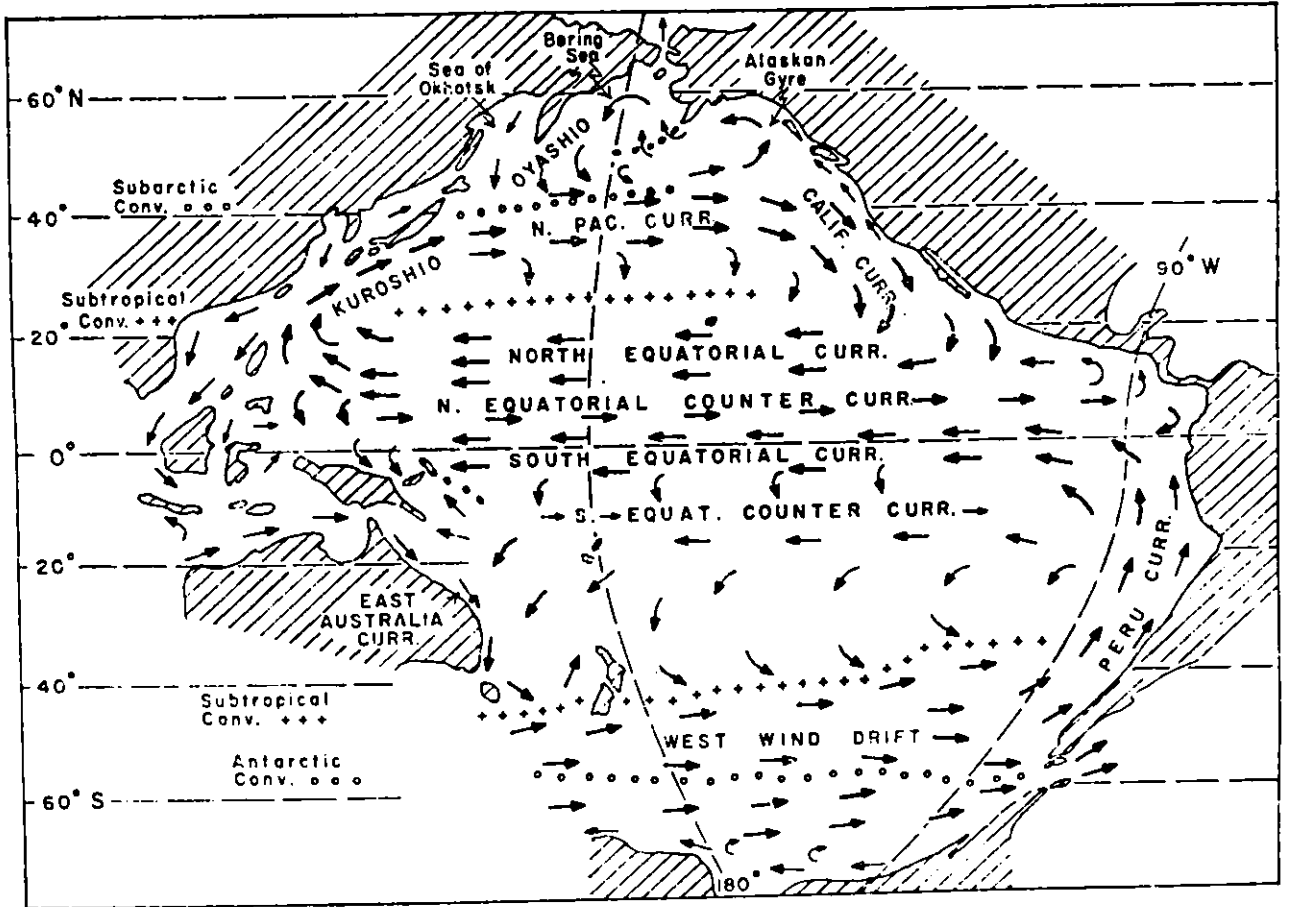


Fig. 45 Circulation of Pacific Ocean surface waters
(From Pickard 1975)

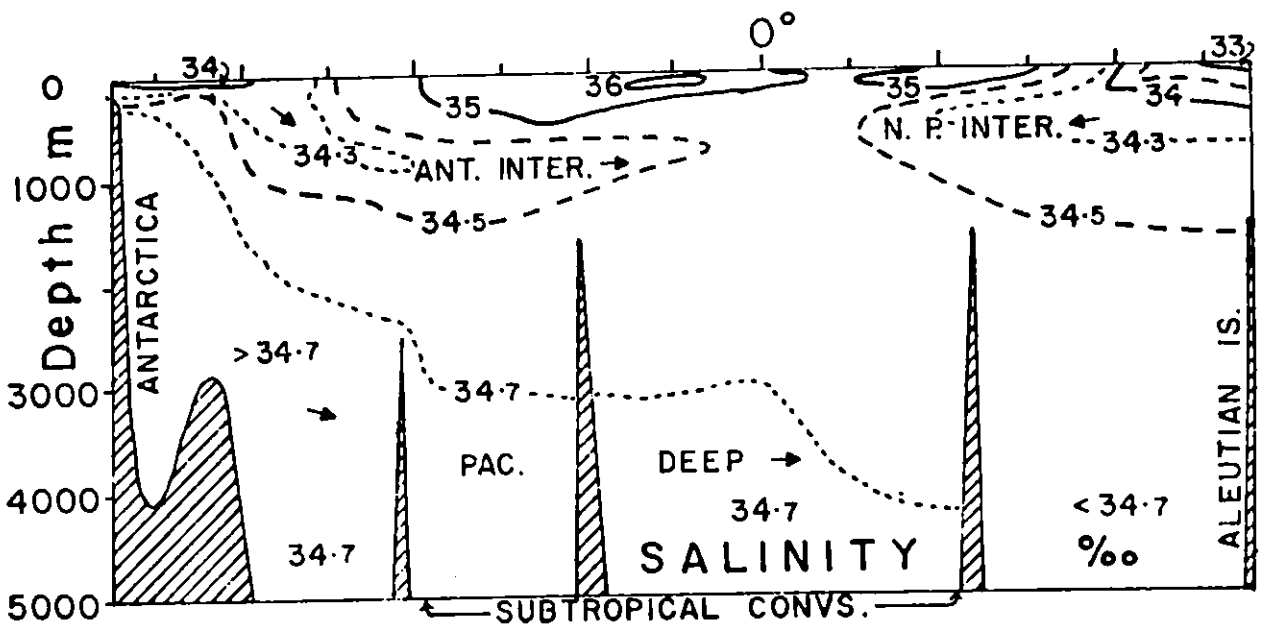


Fig. 46 Distribution of salinity along 175°W in the
Pacific Ocean (from Pickard 1975)

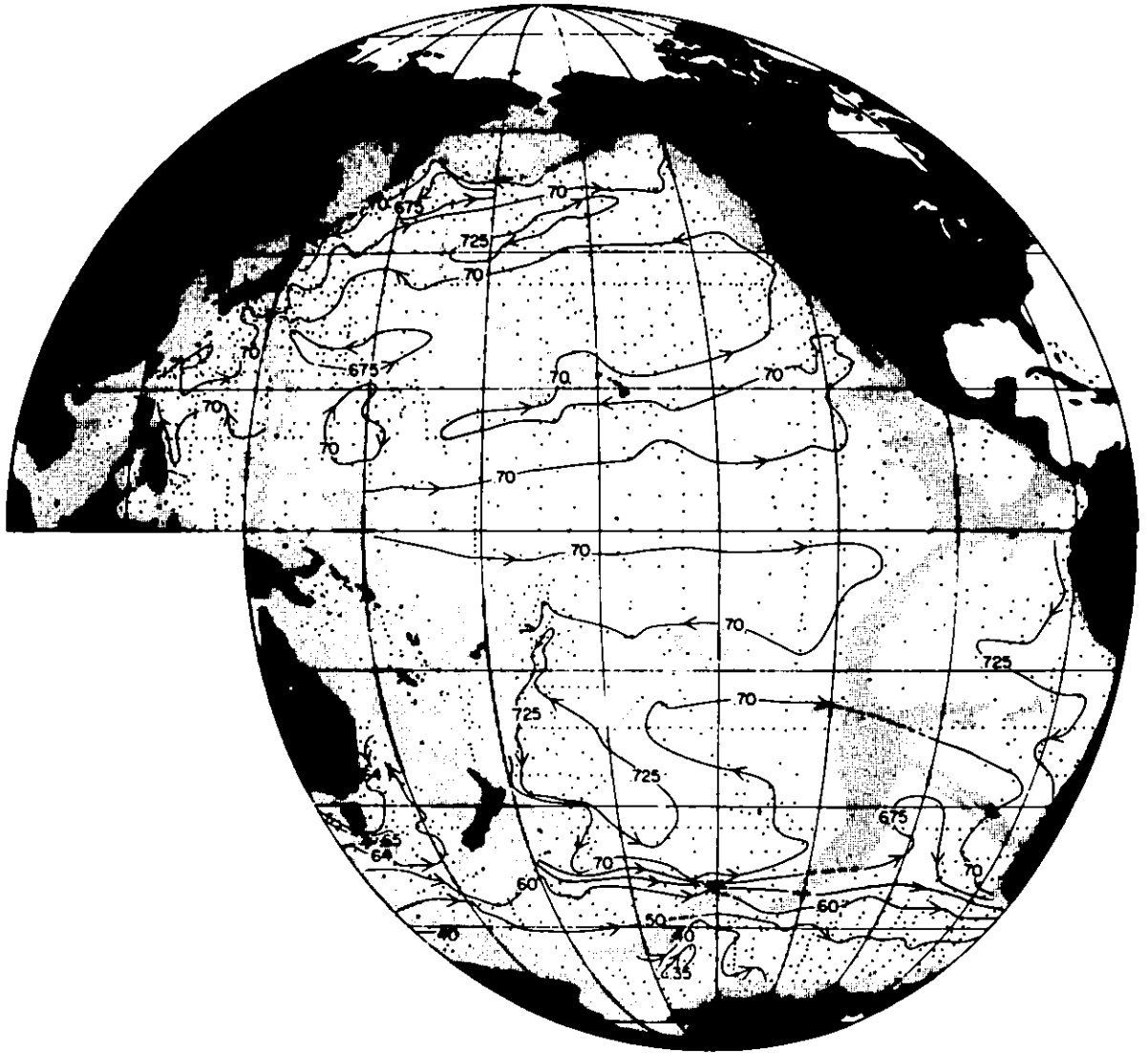


Fig. 47 Steric height at 2000 - 3500 db in dynamic metres ($10\text{m}^2\text{s}^{-2}$ or 10Jkg^{-1}) for the Pacific. (From Reid 1981).

8.3.3 Intermediate Water Masses

Intermediate waters are found below Central waters and extend to approximately 2,000 m. In the S. Pacific, Antarctic Intermediate Water (AAIW) is formed by sub-surface mixing at and north of the Antarctic Convergence (60°S). It is cold (2.2°C), of low salinity (33.8‰) and is rich in oxygen. From the convergence it sinks and flows north (Fig. 46), but is limited in its northward progress by the Pacific Equatorial Water. In the N. Pacific, N. Pacific Intermediate Water extends from 800 m to 2000 m in the west and between 300 and 2000 m in the east. It has a relatively high oxygen content and appears to flow in a clockwise gyre similar to the surface circulation.

8.3.4 Deep Water Masses

The deep water of the Pacific, between about 2000 m and 3500 m, is characterised by very uniform properties and sluggish flow conditions. It is separated from bottom water in the S. Pacific by a 'benthic front' marked by sharp gradients in dissolved oxygen and potential temperature (Craig et al. 1972).

Classical geostrophic flow models (Stommel and Arons 1960) predict a slow southward movement of deep waters away from the western boundary. Recently, however, Reid (1981) has mapped the distribution of salinity, oxygen and the major nutrients on an isopycnal surface at around 3 km and also the steric height at 2000 db relative to 3500 db (Fig. 47). Interpreting this measure of the relative geostrophic shear in terms of the mean flow conditions (away from the western boundary) results in a circulation scheme consistent with the associated distributions of salinity and the non-conservative species. A cyclonic gyre centred at approximately 10°S and an anticyclonic gyre between 10°N and 20°N are the main features of the deep tropical circulation, with an eastwards flow in the equatorial zone (Fig. 47).

CHAPTER 9 CHEMICAL FLUXES TO THE SEDIMENT-WATER INTERFACE

9.1 Introduction

Sinking particulates represent nascent sedimentary material and as such exert a fundamental control on sediment chemistry. Chemical differences between particulates and sediments are indicative of early diagenetic processes which influence the chemistry of the water column, sediments and ferromanganese nodules.

It is commonly thought that nodules underlying high productivity surface waters are enriched in Mn, Cu, Ni and Zn through an enhanced supply of these metals associated with biogenic material (Greenslate et al. 1973, Cronan 1975, Calvert and Price 1977, Pautot and Melguen 1979). Chemical fluxes associated with each biogenic phase (organic matter, opal, calcite, faecal material) may be calculated by multiplying the chemical composition of each phase by its vertical mass flux. Chemical compositions may be determined by the filtration of seawater and analysis of the reported solid fractions (Spencer et al. 1972, Krishnaswami and Sarin 1976), by analysis of plankton tow hauls (Martin and Knauer 1973) or by analysis of scrupulously cleaned phases from surface sediments (Boyle 1981, Elderfield et al. 1981). Direct measurements of particulate flux have recently been made using sediment traps (Wiebe et al. 1976, Spencer et al. 1978, Cobler and Dymond 1980, Honjo 1980, Deuser et al. 1981, Wefer et al. 1982). Here these data are combined to compare the metal fluxes associated with each phase with the metal accumulation rates in S. Pacific sediments and nodules.

9.2 Metal contents of particulate phases

Four potential metal carrier phases are considered in the present analysis:- organic soft parts, opal, calcite and faecal material. Few analyses of individual phases are available in the literature, which in particular precludes an examination of natural variability between

species and changes which may occur as metals are cycled through biological systems. Existing data, however, allows order of magnitude calculations or better to be made.

9.2.1 Organic soft parts

Whilst Martin and Knauer (1973) give trace element data for phytoplankton from Monterey Bay and zooplankton from the East Pacific, they do not include organic carbon (C_{org}) analyses. Landing and Bruland (1980) subsequently analysed the same phytoplankton for C_{org} , and, correcting for aluminosilicates using Taylor's (1964) values for continental crust, determined Mn/C atom ratios (Table 32). Similarly, Mn/C ratios were calculated for the zooplankton assuming a value of 0.35g C per gram dry weight of zooplankton. Assuming all the Al in Martin and Knauer's (1973) analyses to be present in detrital phases, I have calculated the aluminosilicate-corrected metal contents of the plankton and normalised them to Mn (Table 32). Metal/C atom ratios were then determined using Landing and Bruland's Mn/C atom ratio (Table 32). Data for Ti and Co are upper values, since these elements were below analytical detection limits.

9.2.2 Calcite

When considering metal fluxes associated with skeletal material, it is important to differentiate between lattice-locked metals and those present either as adsorbed phases or as trapped oxide flocs (Turekian et al. 1973). Boyle (1981) has measured the metal/Ca ratios of scrupulously cleaned foraminifera tests from sediment cores, the upper limits of which are given in Table 33.

9.2.3 Opal

Martin and Knauer (1973) have reported the concentrations of metals in siliceous frustules separated from

organic and adsorbed phases by oxidation with perchloric and nitric acids and hydrogen peroxide (Table 33). Ni was not detected; since it is possible that the severity of the acid treatment leached Ni from the opaline structure, the quoted Ni value is taken from the whole phytoplankton analyses and as such should be regarded as an upper limit. Similarly, the treatment may have leached other metals; the values quoted for these should therefore be regarded as minimum values.

Table 32 Metal/Mn and metal/C ratios for Monterey Bay phytoplankton and Monterey - Hawaii zooplankton¹

Metal/Mn					Metal/C		
Monterey phytoplankton n=16		Monterey-Hawaii zooplankton n=9			Phyto-plankton	Zoo-plankton ²	Mean
Mean	S.D.	Mean	S.D.				
Fe	35	25	74	47	4.9×10^{-4}	4.0×10^{-4}	4.5×10^{-4}
Cu	1.2	1.0	3.8	2.5	1.7×10^{-5}	2.1×10^{-5}	1.9×10^{-5}
Ni	0.44	0.19	2.0	0.6	6.2×10^{-6}	1.1×10^{-5}	8.6×10^{-6}
Pb	1.0	2.1	1.6	1.1	1.4×10^{-5}	8.6×10^{-6}	1.1×10^{-5}
Zn	4.5	3.3	48	25	6.3×10^{-5}	2.6×10^{-4}	1.6×10^{-4}
Co	<0.2		<0.2		$< 2.8 \times 10^{-6}$	$< 1.1 \times 10^{-6}$	$< 2 \times 10^{-6}$
Ti	<1		<1		$< 1.4 \times 10^{-5}$	$< 5 \times 10^{-6}$	$< 10^{-5}$
Mn					1.4×10^{-5}	0.5×10^{-5}	10^{-5}

¹ Data from Martin and Knauer (1973) and Landing and Bruland (1980)

² Assuming 0.35g C per gram dry weight of material

9.2.4 Faecal material

Chemical data for faecal material are rare. Fowler (1977) found that fresh euphausiid (zooplankton) faecal pellets were significantly (up to 3 orders of magnitude) enriched in most elements compared to whole organisms (Table 33). Spencer et al. (1978) have analysed faecal

Table 33 Metal/CaCO₃ and metal/SiO₂ ratios of biogenic tests plus the elemental composition of a planktonic euphausiid, its faeces and a deep water faecal pellet

	Metal/ ¹ CaCO ₃	Metal/ ² SiO ₂	Deep faecal ⁴ pellet (ppm)	Fresh euphausiid ⁵ faecal pellet (ppm)	Whole ⁵ euphausiid (ppm)	Faecal pellet/ whole organism
Mn	4 x 10 ⁻⁶	3 x 10 ⁻⁶	2110	243	4.2	58
Fe	8 x 10 ⁻⁶	2.4 x 10 ⁻⁴	21600	24000	64	375
Cu	2 x 10 ⁻⁷	8 x 10 ⁻⁶	650	226	48	5
Ni	36.5x10 ⁻⁶	31.4x10 ⁻⁵	-	20	0.66	30
Co	-	-	15	3.5	0.18	19
Zn	4 x 10 ⁻⁶	1.2 x 10 ⁻⁵	< 20	950	62	15
Pb	-	-	-	34	1.1	31
Al	-	-	20800	-	-	-
Ti	-	-	1300	-	-	-
Ca	-	-	2.32 x 10 ⁵	-	-	-
Org. C	-	-	1.5 x 10 ⁵	-	-	-

¹ Data from Boyle (1981)

² Data from Martin and Knauer (1973)

³ Data from Sclater et al. (1976). Ni/SiO₂ data computed from whole phytoplankton analysis.

⁴ Data from Spencer et al. (1978)

⁵ Data from Fowler (1977)

pellets collected in a sediment trap at 5367 m in the Sargasso Sea (Table 33). Compared to fresh faecal pellets, these deep pellets are enriched in Mn, Cu + Co, depleted in Zn and have similar Fe contents. In the absence of a greater data base, it is impossible to ascribe the differences to specific causes. However, it may be expected that oxidative and scavenging process during vertical transport will affect the metal contents and possibly the ratios between them.

In subsequent calculations, Spencer et al.'s (1978) data for deep water pellets are used for 2 reasons; firstly they more likely represent the faecal matter reaching the ocean floor, and secondly the chemical data may be corrected for aluminosilicates, thus allowing examination of non-detrital element fluxes.

9.3 Vertical mass fluxes

Only recently have direct measurements of vertical mass fluxes become feasible through the use of sediment traps which are suspended in the water column (Wiebe et al. 1976, Spencer et al. 1978, Cobler and Dymond 1980, Deuser et al. 1981, Wefer et al. 1982). Since no direct flux measurements have been made in the S. Pacific, certain assumptions must be made in order that measured fluxes may be extrapolated to that region (Table 35). These are discussed through the text.

9.3.1 Organic soft parts

Measured fluxes of particulate organic carbon (POC) made below 300 m are shown in Table 34. Whilst higher C_{org} fluxes are associated with higher productivity continental margin (Hinga et al. 1979), equatorial (Cobler and Dymond 1980) and Antarctic waters (Wefer et al. 1982) than low productivity central gyre waters (Spencer et al. 1978, Honjo 1980, Deuser et al. 1981), the percentage of the primary productivity reading the deep (> 2000m)

ocean in both regions is very similar, approximately 1.5-2% (Cobler and Dymond 1980, Honjo 1978). The similarity of the C_{org} fluxes at different deep ocean levels at the same site, at least in some cases (Table 34) allied to Spencer et al's (1978) elemental and radiotope data which suggests that 90% of the organic matter in the deep Sargasso Sea is contributed by rapidly settling large particles, suggests that most (98.5%) of the POC produced in the eutrophic zone is oxidised above 2000 m whilst the remaining 1.5% is rapidly transferred to the seafloor.

If we assume that 1.5% of the primary production of C_{org} reaches the seafloor, then primary productivity data allows the calculation of the flux of C_{org} to the sediment-water interface. Koblentz-Mishke et al. (1970) have produced a global map of ocean primary productivity. In the study area productivity is less than $55 \mu g C_{cm}^{-2} y^{-1}$ south of $5^{\circ}S$ and rises to an absolute maximum of $135 \mu g C_{cm}^{-2} y^{-1}$ at the equator. The low productivity of S.W. Pacific waters south of approximately $5-10^{\circ}S$ suggests that a more accurate figure for primary productivity may be the $25-35 \mu g C_{cm}^{-2} y^{-1}$ found by Honjo (1978, 1980) in the similarly low productivity Sargasso Sea and North Pacific central gyres.

Since 0.15% of the primary productivity is preserved in the sediment (Heath et al. 1977), 1.35% of the primary productivity is consumed at the sea floor, equal to $30-120 \mu g C_{cm}^{-2} y^{-1}$ in the study area (Table 35).

9.3.2 Calcite

In terms of depth and productivity, the North Central Pacific is similar to the S.W. Pacific to the south of the equatorial high productivity zone (i.e. south of $5-10^{\circ}S$). It is therefore proposed to extrapolate the data from the deep (5582 m) sediment trap deployed there (Honjo 1980) to the S.W. Pacific. Honjo (1980) gives a carbonate flux of $250 \mu g cm^{-2} y^{-1}$; since the study area is essentially all below the CCD, the whole flux is consumed close to the sediment-water interface.

Table 34 Fluxes of particulate organic carbon through
the deep water column

Position	Depth (m)	Flux ($\mu\text{gCcm}^{-2}\text{y}^{-1}$)	Reference
13°30' N 54°00' W	389	245	Wakeham et al. (1980)
	988	146	"
	3755	62	"
	5068	62	"
2°47' N 8°51' W	400	1130	Bishop et al. (1977)
0°36' N 86.6° W	2670	185	Cobler & Dymond (1980)
Sargasso Sea	3200	40-110	Deuser et al. (1981)
38°23' N 69°45' W	3520	560	Hinga et al. (1979)
60°55' S 57°06' W	965	541	Wefer et al. (1982)
	2540	478	"
31°33' N 55°55' W	976	89	Honjo (1980)
	3694	32	"
	5206	3	"
31°34' N 55°03' W	5367	36	"
15°21' N 151°29' W	378	130	Honjo (1980)
	978	20	"
	2778	40	"
	4280	32	"
	5582	24	"

Towards the equator, the calcite flux will be greater. The flux at 2,670 m in the eastern equatorial Pacific is $2750 \mu\text{g cm}^{-2}\text{y}^{-1}$ (Cobler and Dymond 1980), but for two reasons the flux in the equatorial Central Pacific will be lower. Firstly, a comparison of the calcite fluxes at 3200 m and 5367 m in the Sargasso Sea (Deuser et al. 1981, Spencer et al. 1978) and the north Pacific Central gyre (Honjo 1980) suggests that approximately 60% of the calcite flux at 3200 m dissolves in the water column between those levels. The remaining 40% of the Galapagos flux is approximately $1000 \mu\text{g cm}^{-2}\text{y}^{-1}$. Secondly, productivity at 150-170°W is much lower than in the Galapagos region (90°W). Allowing for this, an arbitrary upper limit of $700 \mu\text{gcm}^{-2}\text{y}^{-1}$ is assumed for the calcite flux, which all dissolves close to the sediment-water interface.

9.3.3 Opal

Similar considerations are made for opal as for calcite. Spencer et al. (1978) found that the flux of opal was similar to that of calcite in the deep Sargasso Sea, and I shall use that value for the sub-equatorial S. Pacific ($340 \mu\text{g cm}^{-2}\text{y}^{-1}$). At the equator, the opal flux will be greater, but less than that measured by Cobler and Dymond ($1120 \mu\text{g cm}^{-2}\text{y}^{-1}$). I shall assume a flux of $600 \mu\text{g cm}^{-2}\text{y}^{-1}$.

The equatorial sediments of the S.W. Pacific comprise 10-15% opal (see Section 10.2.3) indicating that not all the opal flux dissolves at the seafloor. Cobler and Dymond (1980) calculate that 80% of the opal flux to the Galapagos seafloor is utilised near the sediment-water interface, suggesting that $480 \mu\text{g cm}^{-2}\text{y}^{-1}$ is utilised in the upper few centimetres of sediment in the equatorial zone of the study area.

9.3.4 Faecal material

Whilst most particles in the water column are within the less than 2 micron size range, the vertical mass flux of particles, defined by the product of particle mass and settling velocity, is dominated by the relatively rare large ($>100 \mu\text{m}$) particles (McCave 1975). McCave has pointed out that the size distributions of particulates suspended in the water column below 200 - 400 m follows a hyperbolic distribution with slopes between -2.4 and -3.6. The cumulative number of particles N greater than diameter d is given by

$$N = ad^{-m}$$

where a and m are constants. McCave (1975) calculates that for particles between 1 and $512 \mu\text{m}$ with $m = 3$, 75% of the vertical mass flux is within the size grades 128 - $512 \mu\text{m}$, whilst these particles account for only 4.6% of the mass concentration. Measured m values quoted by McCave are between 2.4 and 2.8; in these cases the percentage of the vertical flux in the coarser grades is even greater than for $m = 3$.

What form do the important large particles take? Seasonal variations in the flux of both organic carbon and lithogenic particles corresponding with similar variations in primary productivity (Deuser et al. 1981, Honjo 1982) strongly suggest the importance of biological processes. The two most likely contributors are faecal material and 'marine snow'. Faecal material may be defined simply as that material which has been processed through organisms' guts, whilst marine snow comprises large (>0.5 mm) amorphous aggregates most probably cemented by organic mucus (Silver et al. 1978, Alldredge 1979).

Recent observations on material collected in sediment traps suggest that discrete faecal pellets may contribute only 10% of the organic carbon and total mass flux to the deep ocean (Honjo, pers. comm.). Less well aggregated faecal material, perhaps agglutinated into marine snow, may however be a more important vertical carrier of matter than discrete pellets. Bishop et al. (1977) have calculated that 99% of the vertical mass flux at 400 m in the eastern Atlantic is contributed by faecal material and pellets. Of this, only 2% is contributed in discrete pelletal form.

Clearly it is difficult to make a precise estimate of the importance of faecal material in the flux of matter to the deep ocean. In regions such as the S. Pacific which receive a very small supply of lithogenic material, it is however likely to be relatively large. In the calculation of element fluxes I will assume that 75% of the total mass flux is contributed by faecal material.

The best estimate of the mass flux in the S. Pacific may be made using Spencer et al.'s (1978) and Deuser et al.'s (1981) Sargasso Sea data. Spencer et al. (1978) measured a primary flux of $1.0 \text{ mg cm}^{-2} \text{ y}^{-1}$ at 5367 m, compared to Deuser et al.'s (1981) flux of $0.73 - 2.2 \text{ mg cm}^{-2} \text{ y}^{-1}$ at 3200 m. Because suspended particles are in greater concentrations in the Atlantic Ocean than in the central Pacific Ocean (Lisitzin 1972), and because sedimentation rates are lower in the central Pacific (Goldberg et al. 1964, Ku et al. 1968),

I assume a lower primary flux in the sub-equatorial (5-20°S) S. Pacific, $0.5 \text{ mg cm}^{-2} \text{ y}^{-1}$, rising to $1.5 \text{ mg cm}^{-2} \text{ y}^{-1}$ at the equator. This compares with $4.2 \text{ mg cm}^{-2} \text{ y}^{-1}$ at 2670 m in the equatorial East Pacific (Cobler and Dymond 1980). 75% of the flux is contributed by faecal material, i.e. $0.4 - 1.1 \text{ mg cm}^{-2} \text{ y}^{-1}$.

9.4 Element fluxes

Minimum and maximum element fluxes associated with each phase are given in Table 36. The fluxes of Mn, Fe, Cu, Co, Pb, Ti and Al associated with faecal material (Mn_f etc.) are between one and three orders of magnitude greater than for any other phase. The situation for Ni and Zn is less clear-cut. Ni_c (calcite), Ni_o (opal) and Ni_f fluxes are of a similar order, and between five and ten times greater than the Ni_{org} (organic) flux. There is, however, no data for the Ni content of deep water faecal material. As for Mn, Cu and Co, Ni may possibly be enriched in deep water faecal material over fresh faecal material.

Minimum Zn_{org} and Zn_o fluxes are similar, and somewhat greater than Zn_c , whilst Zn_{org} becomes relatively more important in high productivity belts. The greater Zn content of fresh faecal pellets over deep water pellets is in contrast to Mn, Cu and Co. One may hypothesize that this is due to natural variation or that Zn is lost during transit.

9.5 Element accumulation rates in S. Pacific nodules and sediments

Lyle (1981) has found a positive correlation between the measured growth rate of 15 nodules, mainly from the North Pacific, and $E_{Mn}/(E_{Fe})^2$ where E_{Mn} is the concentration of Mn in the nodule. The best-fit regression line for a plot of these parameters is defined by

$$\text{Growth rate} = 16.0 \left[E_{Mn}/(E_{Fe})^2 \right] + 0.448$$

Table 35 Assumed minimum and maximum fluxes of organic carbon, calcite, opal + faecal material in the S.W. Pacific, allowing for material not utilised near the sediment-water interface

	$\mu\text{g cm}^{-2} \text{y}^{-1}$			
	<u>Organic C</u>	<u>Opal</u>	<u>Calcite</u>	<u>Faecal material</u>
Minimum	30	340	340	400
Maximum	120	480	700	1100

Table 36 Minimum and maximum element fluxes associated with organic soft parts, calcite, opal, faecal material corrected for detrital mineral input

			<u>Element flux ($\mu\text{g cm}^{-2} \text{ky}^{-1}$)</u>								
			Mn	Fe	Cu	Ni	Co	Pb	Zn	Ti	Al
Deep water	Organic	min	0.3	14	0.6	0.3	<0.06	0.3	4.8	<0.3	-
		max	1.2	56	2.4	1.2	<0.24	1.2	19	<1.2	-
	Calcite	min	1.0	0.2	0.05	1.6	- ⁴	-	1.0	-	-
		max	4.0	0.8	0.2	6.5	-	-	4.0	-	-
	Opal	min	1.0	81	2.7	4.8	-	-	4.1	31	-
		max	1.4	115	3.8	6.7	-	-	5.8	43	-
	Faecal ¹	min	840	8600	260	-	6	-	8	520	8300
		max	2310	23650	715	-	17	-	22	1430	22800
	Faecal ²	min	97	8200	90	8	1.4	14	380	-	-
		max	267	22550	248	22	4	39	1050	-	-
Fresh	Al- ¹ corrected faecal	min	740	2960	260	³ 0.4	3.6	³ 12	0.8	0	0
		max	2040	8140	715	³ 1.1	9.9	³ 33	2.2	0	0

¹ Data from Spencer et al. (1978)

² Data from Fowler (1977)

³ Pb, Ni data from Fowler (1977)

⁴ = data not available

Table 37 combines this growth rate estimate with element compositional data to give element accumulation rates of equatorial (0-7°S) and subequatorial (7-20°S) nodules from the Penrhyn Basin. Although equatorial nodules contain lower concentrations of Fe, Co, Pb and Ti, they are accumulating these elements as fast as or faster than the sub-equatorial nodules. This is a similar finding to that of Moore et al. (1981) concerning differential element fluxes to the bottom and top sides of a single north equatorial Pacific nodule.

Accumulation rates of Mn, Fe, Cu, Ni, Co and Ti in central Pacific sediments and in their authigenic fractions are taken from Krishnaswami (1976) (Table 38). These elements are accumulating 5-1000 times faster in the sediments than the associated nodules.

Table 37 Mean nodule composition and element accumulation rates of equatorial (0-5°S) and sub-equatorial (5-20°S) nodules in the Penrhyn Basin

	Nodule Composition		(μgcm ⁻² ky ⁻¹) Element accumulation rates ¹	
	Equatorial	Sub-equatorial	Equatorial	Sub-equatorial
Mn	19.3	15.2	110	50
Fe	11.4	15.4	65	50
Cu	0.65	0.22	4	2
Ni	0.79	0.41	5	3
Co	0.22	0.36	1	1
Pb	0.045	0.099	0.2	0.2
Zn	0.099	0.051	0.6	0.4
Ti	0.71	1.10	4	3

¹ assumes ρ_{nodule} = 1.95gcm⁻³ (Greenslate 1977)

A comparison of element supply rates and metal accumulation rates in nodules (Tables 39 and 40) indicates that opal can supply all the Fe, Cu, Ni, Zn and Ti accumulating in nodules. Similarly calcite can supply all the Zn and much of the Ni, whilst organic material can supply all the Pb and Zn, significant proportions of the Fe and Cu, and some Ni. Non-detrital faecal material is the only phase containing sufficient Mn and Co to account for their accumulation rates

Table 38 Mean total and authigenic element accumulation rates in 3 central Pacific sediments¹ and in sub-equatorial Penrhyn Basin nodules, plus element fluxes associated with faecal material²

	Element $\left\{ \begin{array}{c} \text{fluxes} \\ \text{accumul} \end{array} \right\}$ rates ($\mu\text{g cm}^{-2}\text{kg}^{-1}$)					
	Mn	Fe	Cu	Ni	Co	Ti
1. Whole sediment	790	5360	25	13	8	430
2. Authigenic sediment	675	1125	17.4	15.3	6.5	15
3. Sub-equatorial nodules	50	50	2	3	1	3
4. Faecal material ³	840	8600	260	8	6	520
5. Al-corrected faecal material	740	2960	260	0.4	3.6	0
6. Sediment + nodule	840	5410	27	16	9	433
$100 \times \left[\frac{\text{Faecal material}}{(\text{sediment} + \text{nodule})} \right]$	100	160	960	50	66	120
$100 \times \left[\frac{\text{Al-corr. faecal}}{\text{Authigenic sediment}} \right]$	110	260	1490	3	55	0

¹ Data from Krishnaswami (1976):-

Cores:- V18 - 258; 11°52'S 165°45'W

NOVA III 13: 3°56'N 178°47'W

NOVA III 16; 0°14'N 178°8'W

² See text for details

³ Minimum flux. Data from Spencer et al. (1978)

in nodules, and can also supply the requisite Fe, Cu, Pb and Zn. Whilst it cannot apparently account for the Ni accumulation rate, as stressed before, the Ni content of deep water faecal pellets is unknown.

In contrast, the greater accumulation rates of Mn, Fe, Cu, Co and Ti in the sediments can only be supplied by faecal material (Table 38). The other phases can supply only a few percent or less of these elements. A comparison of the faecal element fluxes with their accumulation rates in the sediment (Table 38) shows a reasonably close correspondence for Mn, Fe, Ni, Co and Ti. Cu is supplied in excess by an order of magnitude. Whilst Klinkhammer (1980) has suggested that perhaps 50% of the Cu flux is lost by diffusion into the water column during early diagenesis, allowance for this still leaves a 5-fold excess of input Cu. Overall, however, the close correspondence is encouraging and supports the original tenet that the vertical mass flux is dominated by faecal material. Finally, it is interesting to note that faecal material appears capable of supplying the 'excess Mn' which occurs in pelagic sediments over shale (Bender 1971), although the present data are insufficient to ascertain the ultimate sources of that Mn.

There is a similarly close correspondence between the non-detrital supply of Mn_f and the rate of accumulation of authigenic Mn in the sediment (Table 38), and a moderate correspondence for Fe and Co. Cu is supplied in excess, but only a few percent of the authigenic Ni is derived from faecal material. Bearing in mind the previous comments concerning Ni_f , examination of Tables 36 and 38 indicates that together opal and calcite can account for 50-100% of the Ni in sediments.

Sediment compositional data indicates that Zn accumulates at a similar rate to Cu and Ni. The high fluxes of Zn_{org} , Zn_o and Zn_f suggests that all these phases are capable of accounting for the Zn accumulation rate.

Table 39 Comparison of minimum individual phase element
fluxes to the seabed with metal accumulation rates
in sub-equatorial nodules

Element Phase	(flux/nodule accumulation rate) x 100%							
	Mn	Fe	Cu	Ni	Co	Pb	Zn	Ti
Organic	0.3	28	30	10	<6	150	1200	<10
Calcite	1	0.6	4	73	-	-	350	-
Opal	0.6	160	135	160	-	-	1030	1030
Faecal	1700	17200	13000	270	600	7000	2000	17300
Al-corrected faecal	1500	5900	13000	13	360	6000	200	0

Table 40 Comparison of maximum individual phase element fluxes
to the seabed with metal accumulation rates in
equatorial nodules

Element Phase	(flux/nodule accumulation rate) x 100%							
	Mn	Fe	Cu	Ni	Co	Pb	Zn	Ti
Organic	1	86	60	24	< 24	600	3170	< 30
Calcite	4	1	5	130	-	-	670	-
Opal	1	180	95	130	-	-	580	1080
Faecal	2100	36400	17900	440	1700	19500	3700	35800
Al-corrected faecal	1850	12500	17900	22	990	16500	370	0

9.6 Summary

Combining element compositional data with mass fluxes of the biogenic phases opal, calcite, organic soft parts and faecal material allows chemical fluxes to the sediment-water interface to be calculated. This type of analysis suggests that faecal material may well be an important vertical carrier of both mass and metals. It is envisaged that eutrophic zone organisms concentrate metals into their faeces which are then rapidly transferred to the seafloor. Fluxes of Mn_f , Fe_f , Cu_f , Co_f , Pb_f , Ti_f and Al_f are 1-3 orders of magnitude greater than fluxes with any other biogenic phase, although opal, calcite and organic matter supply important quantities of Ni and Zn.

Whilst opal can supply sufficient Fe, Cu, Ni, Zn and Ti, calcite sufficient Zn, and organic matter sufficient Pb and Zn to account for the accumulation rate of these metals in nodules, only faecal material can contribute adequate Mn and Co. It can also supply the Fe, Cu, Pb and Zn. In contrast the greater accumulation rates of Mn, Fe, Cu, Ni, Co and Ti in sediments can only be supplied by faecal material; other phases can supply only a few percent. The reasonable agreement of the Mn_f , Fe_f , Ni_f , Co_f and Ti_f fluxes with their accumulation rates in sediments is encouraging support for faecal material as an important vertical carrier of metals through the water column.

Chapter 10 Sedimentology and Mineralogy

10.1 Introduction

A total of 72 surface sediments and four from 50 cm depth were obtained from the area extending from 0-20°S, 145 - 175°W (Fig. 48). Samples identified by K1, K2, K3, C1 and C2 (Appendix 2) were collected by a modified free-fall grab during the 1980 CCOP/SOPAC cruises, whilst the rest were obtained from the tops of existing cores stored at the Hawaii Institute of Geophysics, Scripps Institution of Oceanography and Lamont Doherty Geological Observatory.

Each sediment was examined using smear slides and classified according to the DSDP recommendations (Burns, Andrews et al. 1973). In this classification the major constituent is listed last and represents more than 25% of the sediment. Components of decreasing importance are listed progressively earlier in the classification, with divisions representing 10-25% of the bulk sediment (rich) and 2-10% (bearing). For example, 'calcite bearing siliceous mud' represents a sediment containing 2-10% calcite and more than 25% each of siliceous microfossils and mud (clay minerals, fine-grained quartz and feldspar). The classification 'ooze' is used to describe a sediment in which one constituent dominates the assemblage to the extent that no other particle type exceeds 25%. Sediment classifications are given in Appendix 2.

Selected sediments were examined on a scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser unit. Mineralogical determinations on certain bulk sediments were made by X-ray diffraction (XRD) and on the <2 µm fractions of the majority of samples. Additionally, selected < 0.5 µm fractions were mineralogically examined by XRD and chemically analysed.

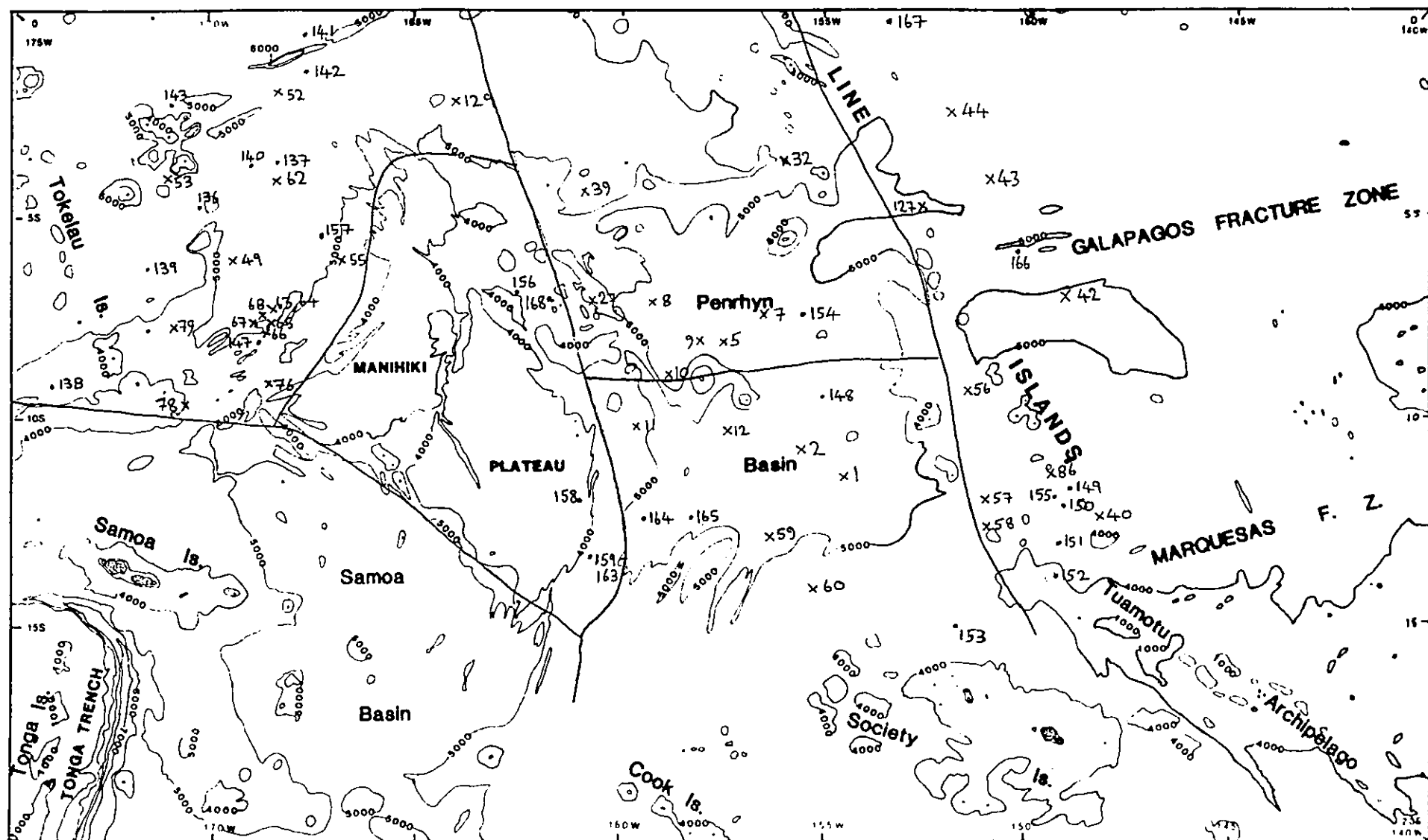


Fig. 48 Sediment sample locations showing the division of the region into separate areas—the Tokelau, the N. and S. Penrhyn Basins, the Manihiki Plateau and the East Line Islands area. Sites at which nodules were also found are marked with an 'x'. Numbers refer to stations listed in Appendix 4.

10.2 Sediment components

10.2.1 Calcite

Most calcite is present as jagged grains up to 200 μm diameter, but generally smaller than 100 μm , which are most probably fragments of foraminifera tests. Nannofossils, whilst common in most carbonate-bearing sediments, are quantitatively less important than foraminifera. Only in sediments Cl-1, V18-267, V18-275 and V18-279 do nannofossils dominate foraminifera. Discoasters were observed in low abundances in a few samples (Appendix 2).

Calcite rhombs were observed in samples K2-13 and K2-14 (Plate 6). These are interpreted as being formed by the recrystallisation of microfossils in slowly accumulating sediments forming just above the CCD.

10.2.2 Carbonate dissolution

The plot of sedimentary CaCO_3 content versus water depth (Fig. 49) indicates that the sedimentary lysocline (Berger 1975) occurs around 4600 m in the S.W. equatorial Pacific and that the CCD lies near to 4,900 m, in good agreement with previous estimates (Berger et al. 1976). The plot is complicated by the occurrence of calcite-bearing sediments below 4,900 m, which have probably been redeposited from shallower depths (e.g. Moore et al. 1973, Orwig 1981), and by calcite-poor sediments at lesser depths, which have a large volcanoclastic component.

Unfortunately changes in the calcite content of a sediment tell us little about carbonate dissolution because any reasonable solution-depth profile produces a 'sudden' decrease in calcite content at the level where the amount of calcite becomes comparable to the amount of non-carbonate diluents (Berger 1971). Whilst both chemical data (Broecker and Takahashi 1978) and observations from sediment traps (Honjo 1980, Thunell and Honjo 1981) suggest that the sedimentary lysocline may represent a depth of level of accelerated dissolution, comparison of the flux of CaCO_3 with its sedimentary accumulation rate

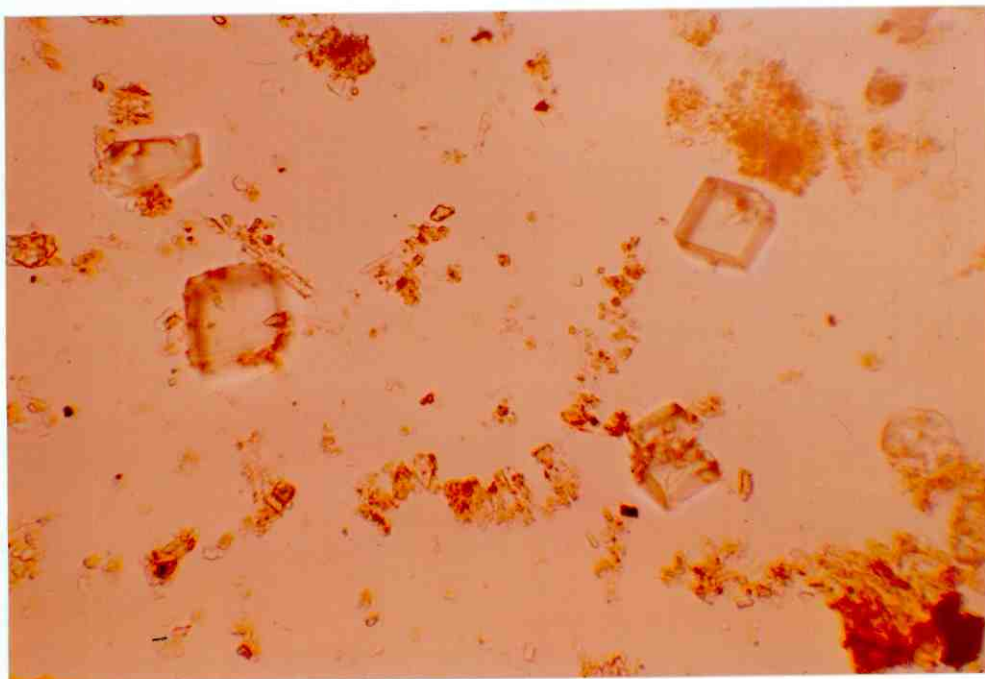


Plate 6. Photomicrograph of sediment sample K2-13, showing recrystallised calcite rhombs, and dark irregularly shaped ferromanganese oxide grains. 720 X.

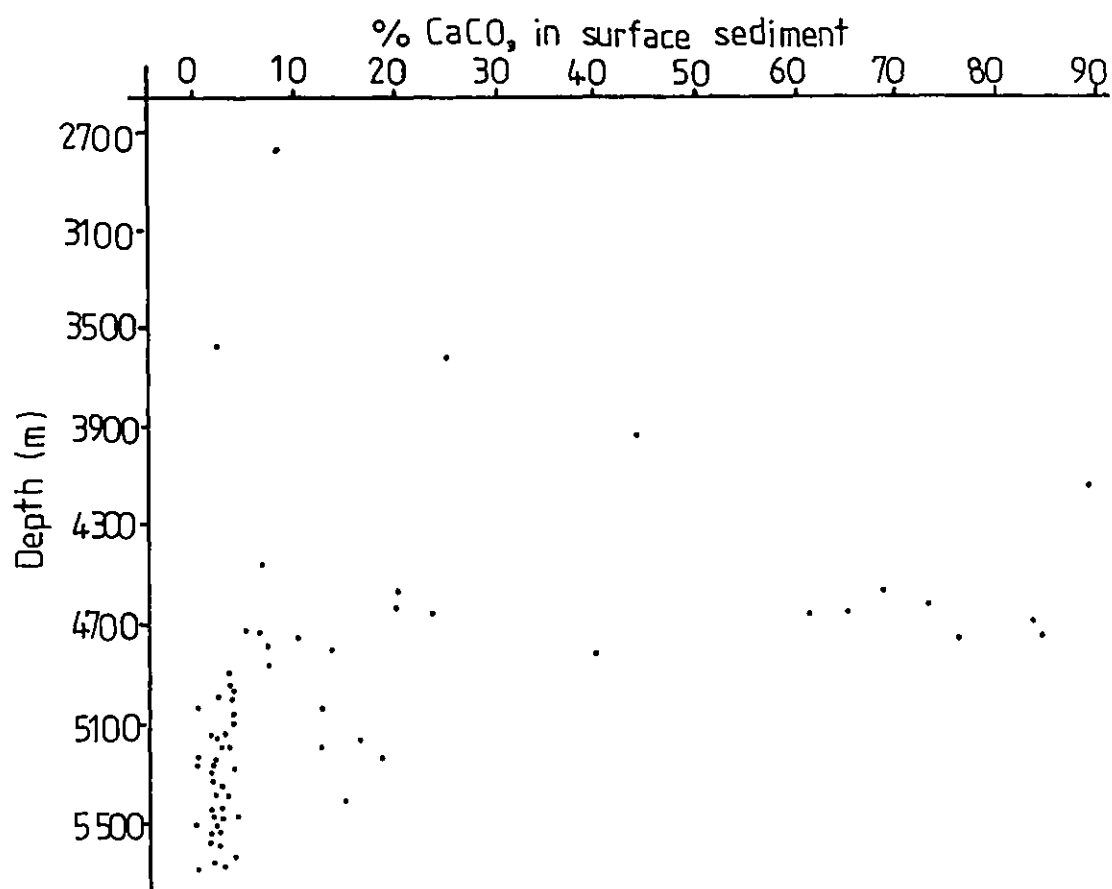


Fig. 49 The distribution of CaCO_3 with depth in S.W. Pacific surface sediments

(Cobler and Dymond 1980) indicates that significant dissolution occurs above the lysocline. The only recognisable calcareous microfossil in the present suite of sediments is the solution resistant *Globorotalia* (Adelseck and Berger 1975), indicating significant levels of dissolution above at least 4100 m.

10.2.3 Siliceous microfossils

The distribution of biogenic silica in the S.W. Pacific sediments (Fig. 50) follows the precept that opaline sediments occur under areas of high surface water productivity where the CCD is above the seabed (Lisitzin 1972). Thus whilst

the sediments are in general poorly siliceous, with values rarely exceeding 20%, the greatest abundances of opal occur in the equatorial zone of the northern Penrhyn Basin and Tokelau regions, areas which lie below the CCD where productivity is moderately high (Schmithüsen 1976). Although productivity increases eastwards in the Pacific (Koblentz-Mishke et al. 1970) the ocean crust also shoals eastwards until the equatorial CCD intersects the seabed in the vicinity of LIA. Further east, carbonate dilutes the concentration of siliceous tests. Southwards, the abundance of siliceous microfossils decreases rapidly until they are virtually absent south of approximately 10°S .

Certain sediments from the Samoan Passage (SOTW X IFFA, 2FFD, 3FFA, 4FFB, 5FFA) contain higher abundances of opal than predicted by the above model. Whilst this may be a genuine anomaly, a second hypothesis is that the fossils have been redeposited from shallower depths by turbidity currents which are known to sweep the area (Lonsdale 1981).

The siliceous fossil assemblage consists of radiolarians, diatoms, sponge spicules and rare silicoflagellates, with predominant radiolaria. The assemblage is generally in an advanced state of dissolution (Plates 7, 8, 10-16). Commonly only siliceous fragments are seen, until in poorly siliceous sediments only particularly robust radiolaria and solution-resistant sponge spicules and orosphaerid fragments are seen (Johnson 1974).

Accompanying the dissolution there is an apparent replacement of the radiolaria by clays and/or Fe oxides, which may be observed both by the exceptionally close association of these components (Plates 7 & 8), and by the occurrence of delicate authigenic clay fabrics closely associated with dissolving biogenic silica (Plates 11-16).

Whilst dissolution of biogenic silica can occur within the water column, sediment trap studies (Honjo 1978, Cobler and Dymond 1980) suggest both that well preserved siliceous



Plate 7. Photomicrograph of sediment sample K3-2, showing closely associated Fe oxyhydroxides, clay minerals and biogenic silica. 720 X.



Plate 8. Photomicrograph of sediment sample K3-7, showing the close association of clay minerals and a radiolarian in an advanced state of dissolution. 1440 X.

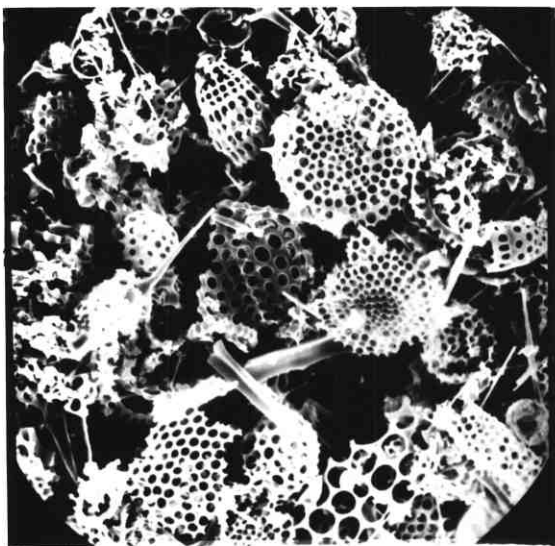


Plate 9 M70-34 Diverse siliceous microfossil assemblage, showing fragmentation and early signs of dissolution. 365X

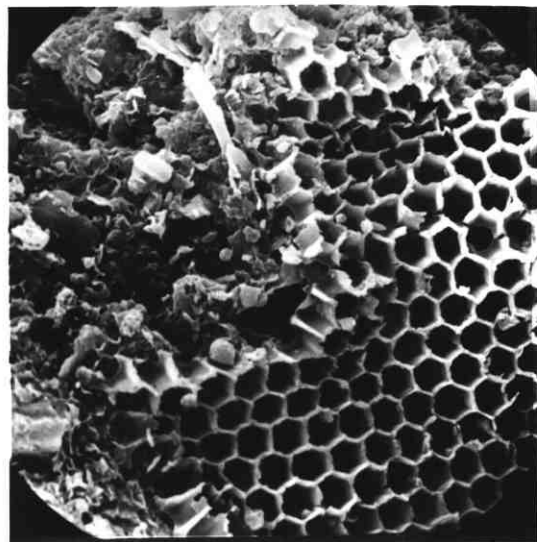


Plate 10 C1-13. Note ragged edges to pores. 2500X

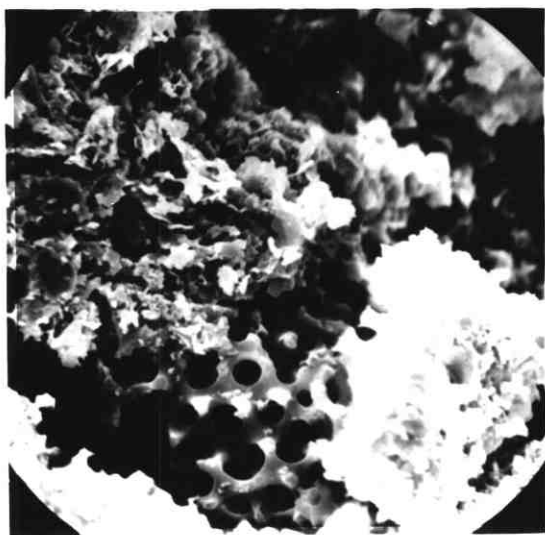


Plate 11 C1-13. Advanced state of dissolution, with replacement by delicate authigenic clays. 1000X

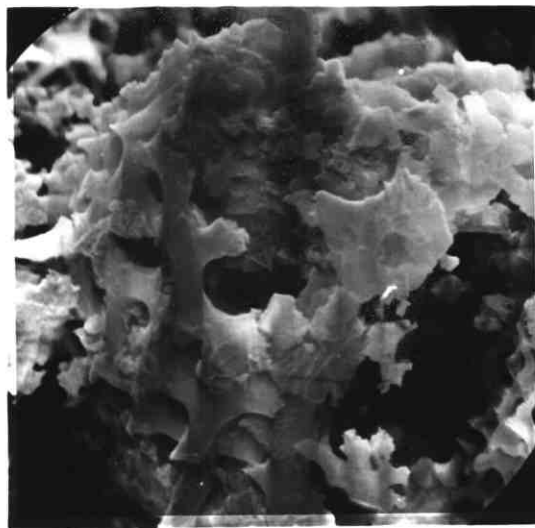


Plate 12 K3-2. Infilling of radiolarian by authigenic clay. 1650X

Plates 9-12. Scanning electron micrographs of surface sediments showing radiolaria undergoing progressive dissolution and replacement by authigenic clays.

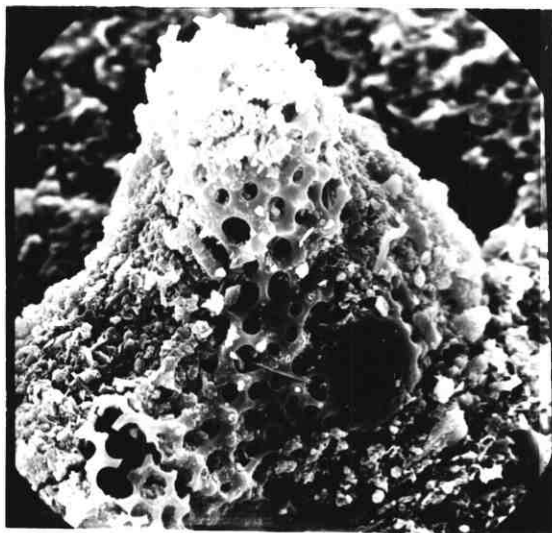


Plate 13 Cl-10 Globule at lower right comprises very pure Al (oxyhydroxide ?) 1100X

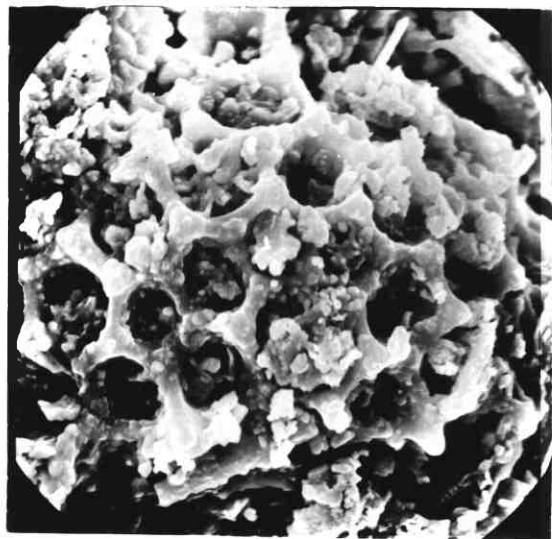


Plate 14 STYX 35G. 1450X

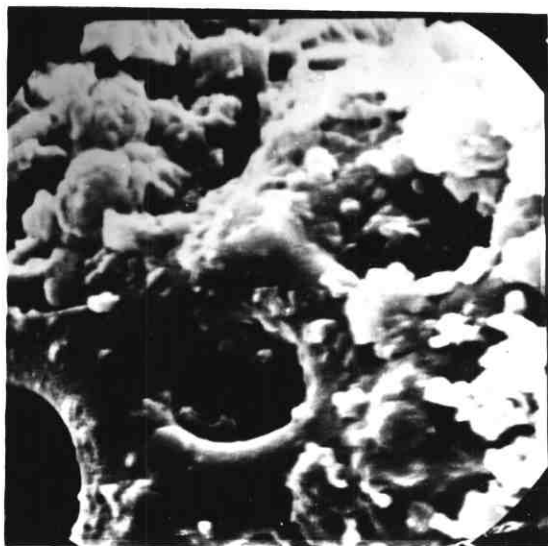


Plate 15 STYX 35G. Enlargement of Plate 14. 3300X

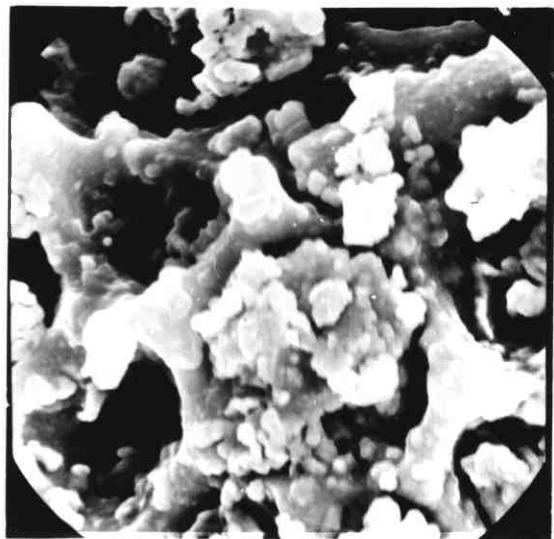


Plate 16 Cl-10. 8300X.

Plates 13-16. Scanning electron micrographs of surface sediment radiolaria in advanced states of dissolution, showing replacement by authigenic clays. Magnification increases from Fig. 13 to Fig. 16.

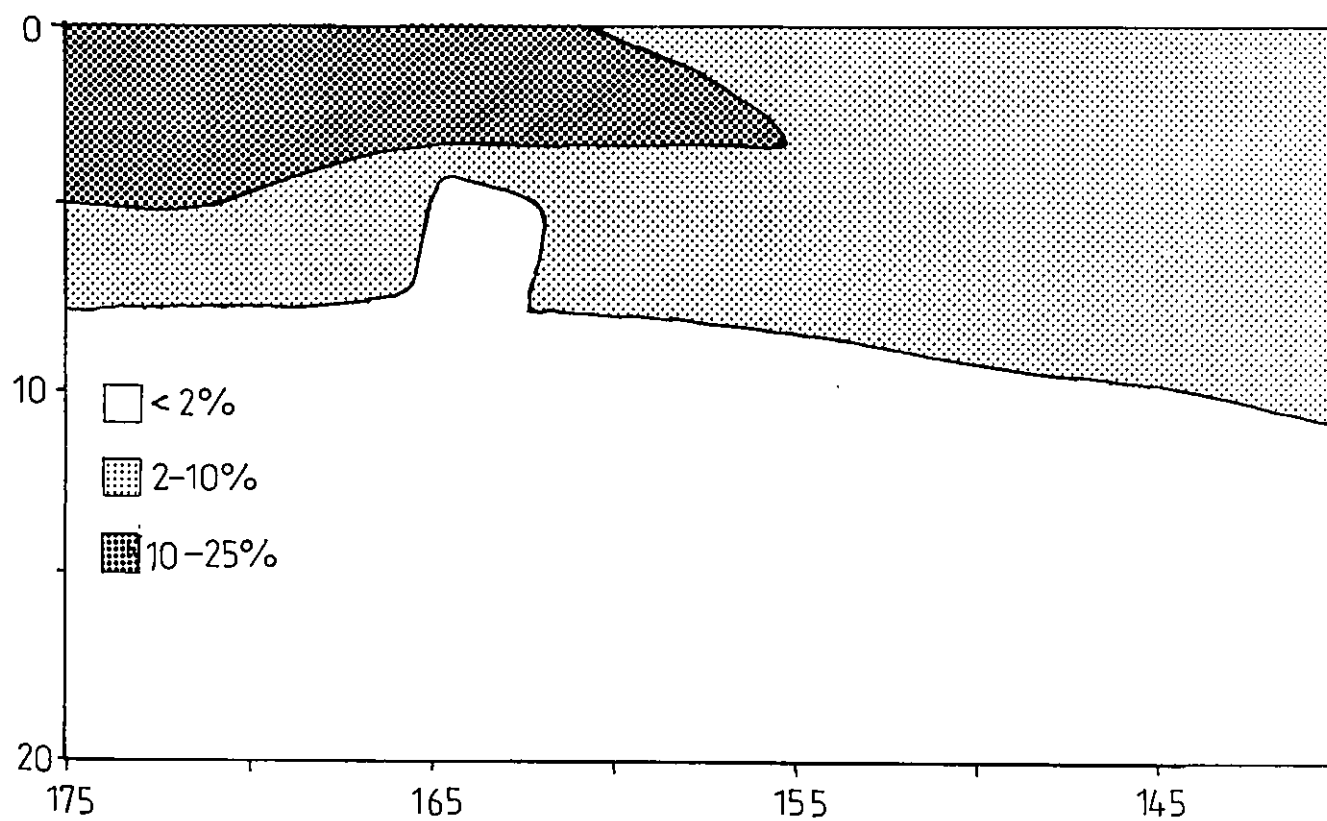


Fig.50 Distribution of biogenic silica in surface sediments.

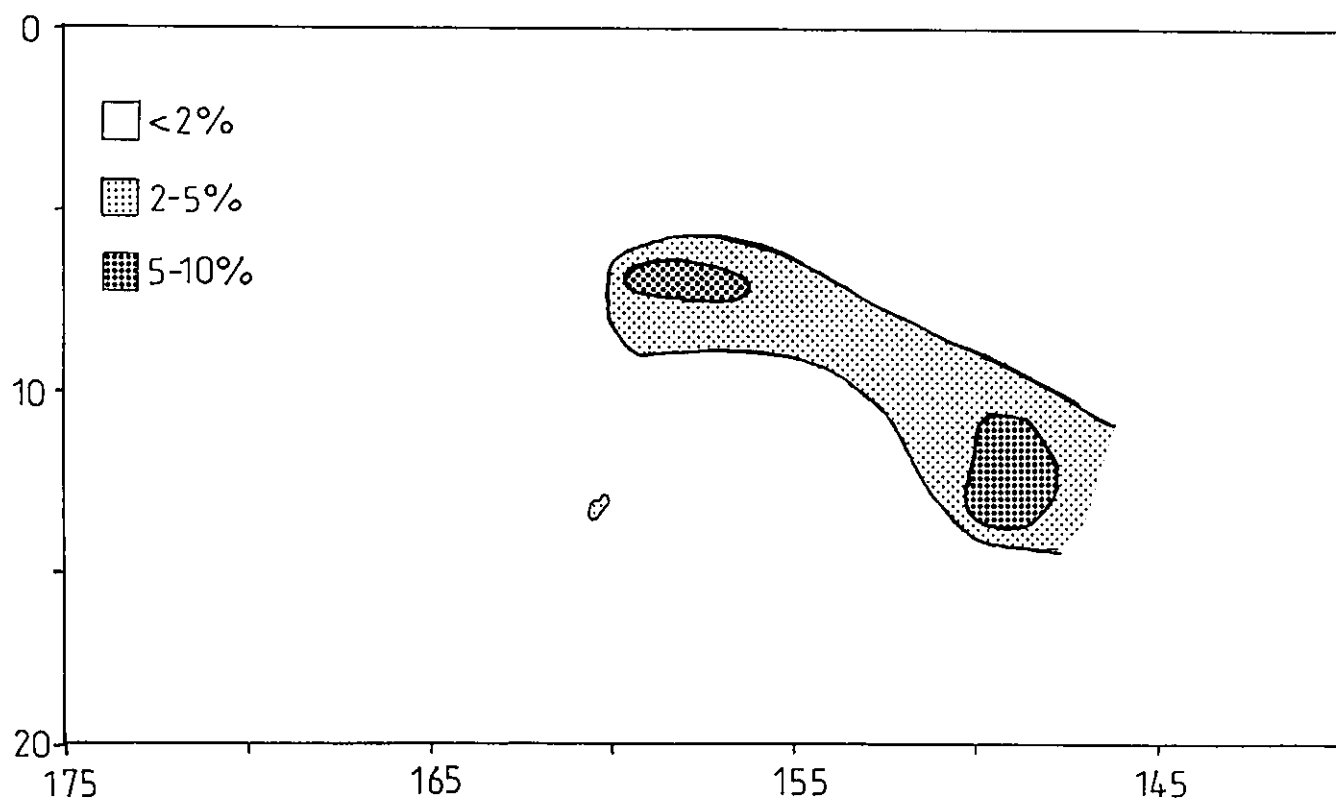


Fig.51 Distribution of fish debris in surface sediments.

microfossils reach the seabed and that significant dissolution occurs in the upper few centimetres of sediment. The advanced state of decay of microfossils in many surface sediments indicates that dissolution occurs at the sediment-water interface. Further, examination of core K1-2, K1-4, K1-5 and K1-6 suggests that dissolution is a continuing process down core.

The best-preserved assemblages occur in sediments which are silica-rich (e.g. M70-34, STYX 35, Plate 9). The enhanced preservation may be due to an increased concentration of dissolved silica in the sediment pore waters (Hurd 1972).

10.2.4 Fish Debris

Whilst essentially absent over much of the region, phosphatic fish debris is common in a NW - SE band between the North Penrhyn Basin and the northern end of the Tuamotu Archipelago, reaching abundances of 5-7% (Fig. 51). Typically, it consists of white or slightly green irregular grains up to 120 μm diameter. These are weakly anisotropic and may have pronounced surface textures (Plate 17).

Bischoff et al. (1979) have suggested that P is a good index of sediment maturity, a term which is essentially a measure of the timespan a particle resides at or near the sediment-water interface. Since fish debris represents an important phosphatic phase in the sediment, it is inferred that it too is a good index of low sedimentation rates. Analyses of the $< 0.5 \mu\text{m}$ fractions of some sediments (Table 42) show a strong correlation between Ca and P, the concentrations of which are greatest in sediments containing significant amounts of fish debris (C1-13, C1-15, K2-11). Hein et al. (1979a) have suggested that fish debris may dissolve and reprecipitate as prismatic apatite crystals. Such authigenic reactions will be most pronounced in slowly accumulating sediments, suggesting a strong relationship between fish debris, P and sediment accumulation rates.

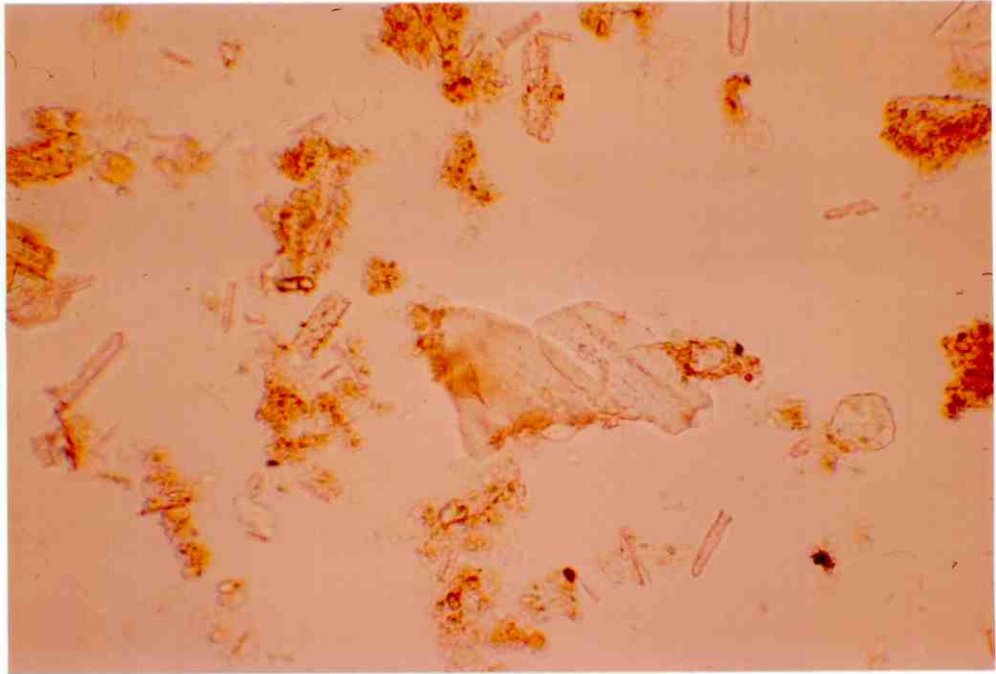


Plate 17. Photomicrograph of sediment sample K2-11, showing phosphatic fish debris, and single laths of phillipsite. 720 X.



Plate 18. Photomicrograph of sample K2-1, showing a development of a phillipsite twin through the replacement of volcanic glass(?). 720 X.

Further support for the use of fish debris as an indicator of low sedimentation rates is derived from the closely similar distributions of it and Mn (Fig. 65), since Krishnaswami (1976) has observed that there is an inverse relation between Mn abundance and sedimentation rates in Central Pacific sediments.

10.2.5 Zeolite

Phillipsite was the only zeolite recognised with certainty in the S.W. Pacific sediments. It occurs dominantly as delicate, single laths (Plate 17) ranging in length from 10-200 μm , but generally less than 100 μm . Rarer phillipsite twins and occasional aggregates comprising several laths and/or twins occur through the area (Plates 18-21).

Phillipsite is abundant throughout the Penrhyn Basin (PB) and Eastern Line Islands (ELI) region, comprising upto 50% of certain sediments to the north of the Tuamotu Archipelago (Fig. 52). In contrast, it occurs only in trace quantities in the Tokelau sediments. Although more common and widespread than fish debris, the pattern of phillipsite nevertheless resembles that of fish debris, from which it is inferred that phillipsite is most abundant in slowly accumulating sediments.

Since phillipsite is a known weathering product of basaltic glass and palagonite (Rex 1967), it is commonly suggested that much of the phillipsite in deep sea sediments is derived in this way (e.g. Bonatti 1963, Kastner and Stonecipher 1977). In the present samples, however, it is the exception to observe phillipsite replacing glass or palagonite, and indeed most commonly no obvious precursor is seen. Further, there is an antipathetic relation between the distributions of phillipsite (Fig. 52) and volcanic glass (Fig. 53). The observation that phillipsite is most abundant in the most slowly accumulating sediments suggests that the dominant mechanism for its formation is by nucleation and growth with no need for precursors. Whilst the silica for its formation may be supplied by

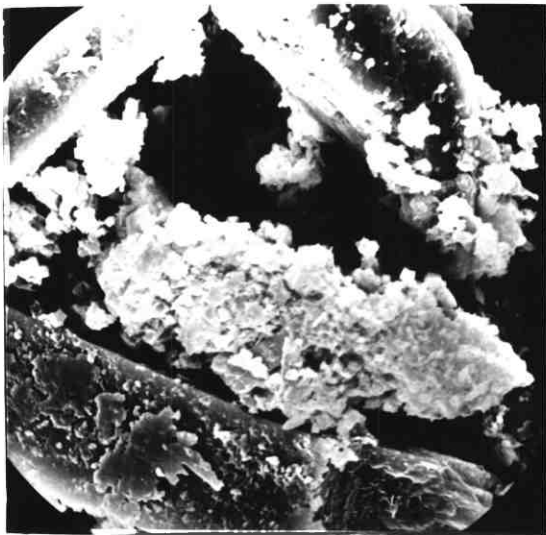


Plate 19 AMPH 117P. Single phillipsite crystals. Central crystal appears to be undergoing dissolution and transformation to delicate clay fabrics. 2500X.



Plate 20 K2-11. Etched phillipsite twin. 1100X.

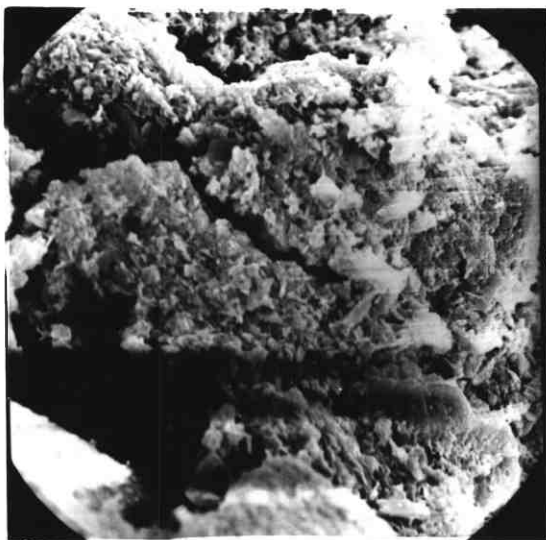


Plate 21 Cl-16 Authigenic clays developing on zeolite and fragment of volcanic(?) material. 830X



Plate 22 Cl-16. Enlargement of Plate 21. 2660X.

Plates 19-22. Scanning electron micrographs of phillipsite (19, 20) and a volcanic(?) fragment (21, 22) with associated authigenic clays.

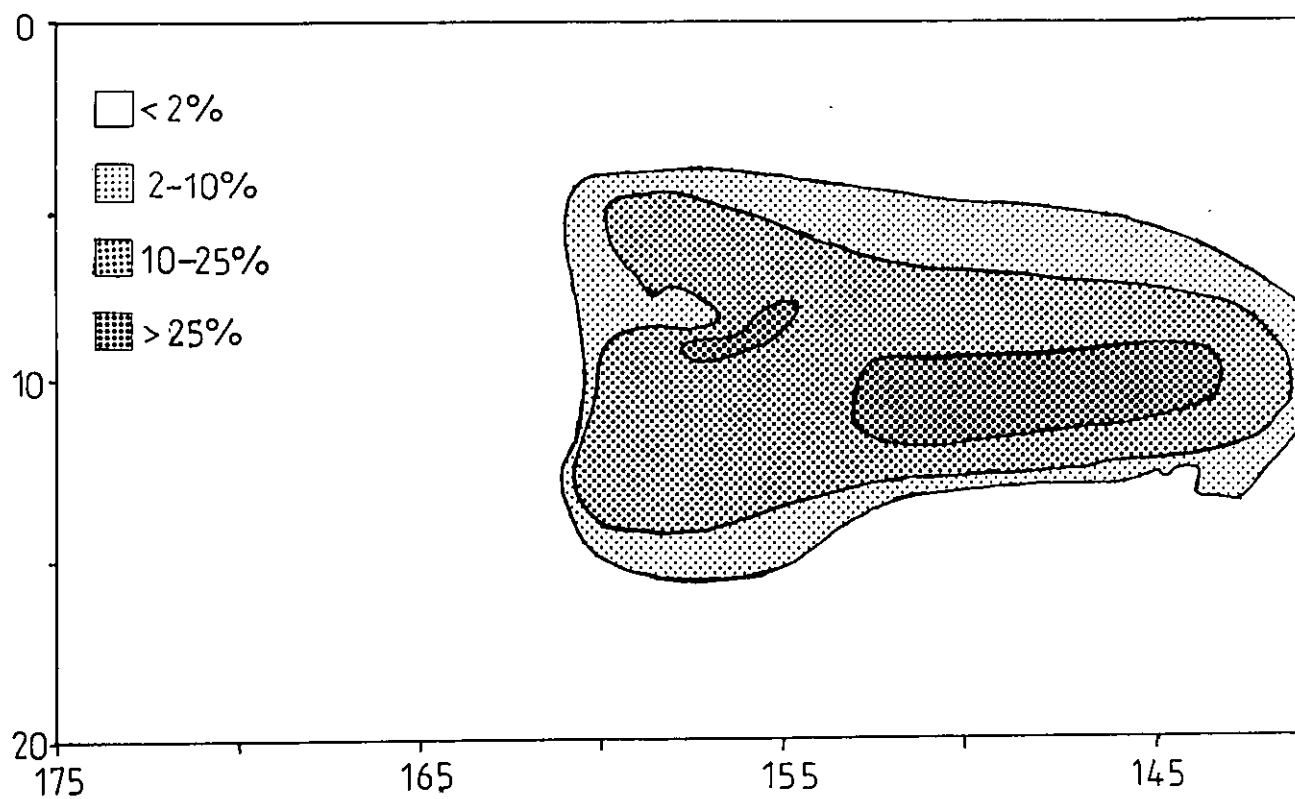


Fig. 52 Distribution of phillipsite in surface sediments.

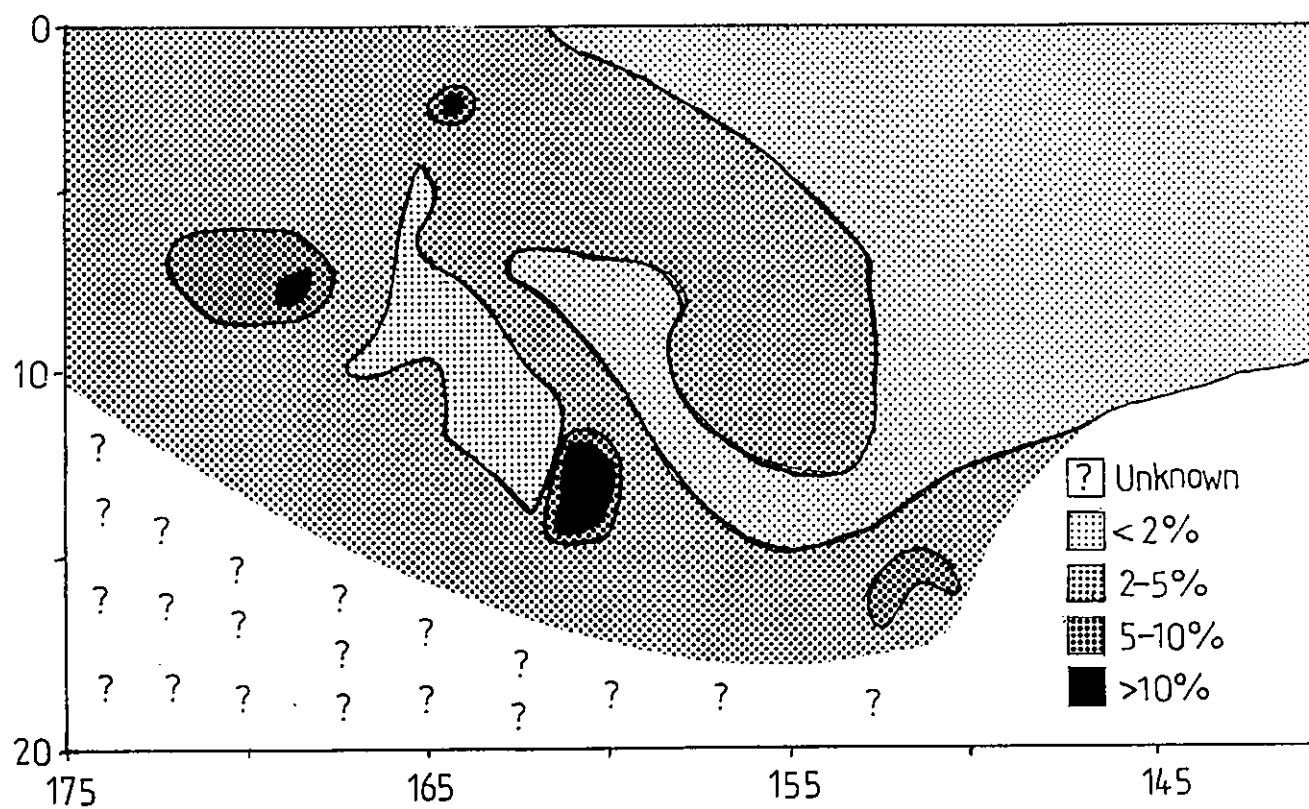


Fig. 53 Distribution of volcanic glass in surface sediments.

dissolving siliceous microfossils (Arrhenius 1963), the source of the Al is more problematical. Some may be supplied in association with the biogenic silica (Hydes 1979, Stoffyn and Mackenzie 1982); in addition there is abundant Al present in the oxide fraction of the sediments (Section 11.5). In some way the Al must be liberated from the oxide phase to form the phillipsite, which is essentially a Na-Al silicate.

10.2.6 Volcanic glass

Whilst volcanic glass is observed in most samples, its patchy regional distribution (Fig. 53) suggests the importance of localised volcanogenic input. Glass is thus abundant close to the Samoan and Society Islands, both of which have been volcanically active in Pleistocene times, and in the vicinity of seamounts (C1-7, M70-17) and on the south-eastern slopes of the Manihiki Plateau, where slumping of volcanic debris is likely to occur.

The close correspondence between the distributions of glass and TiO_2 (Figs. 53 and 62) coupled with the high concentration of TiO_2 in the glass-rich sediments of the Samoan Passage (upto 2.4%) suggests that glass in the Tokelau region is derived from the TiO_2 -rich Samoan volcanics (3.7%, Natland 1980) rather than the relatively TiO_2 -depleted Tongan volcanics (1.5%, Ewart et al. 1977. See also Section 11.3).

Conversely, the volcanic sediments close to the Manihiki Plateau generally contain less than 1% TiO_2 , reflecting the low Ti contents of the Manihiki tholeiitic basalts (Jackson et al. 1976).

Most glass is less than 50 μm in diameter. It varies in colour from clear through fawn and green to yellow, orange and brown (Plates 23 & 24). Most is severely weathered (or palagonitised), appearing pitted, with an irregular but smooth outline and exhibiting complex extinction patterns under crossed nicols. Whilst being cognitive of the natural colour range of volcanic glass, the



Plate 23. Photomicrograph of sediment sample CATO 10, showing orange shards of volcanic glass. 360 X.



Plate 24. Photomicrograph of sediment sample KK72-37, showing a fragment of volcanic glass in an advanced state of weathering and the probable formation of Fe oxide-rich globules around its periphery. 1440 X.

observation that the orange is also in the most advanced state of weathering is consistent with Hart's (1973) work suggesting that Fe is oxidised and forms oxyhydroxides during the weathering process. Further, both phillipsite (Plate 18) and authigenic clays (Plate 21) are forming as a result of weathering.

10.2.7 Ferromanganese oxides

In the present samples Fe-Mn oxides occur in four morphological categories:-

1. Submicroscopic brown particles associated mainly with fine-grained clays (Plate 25).
2. Black, circular, sub-circular or botryoidal grains 5-20 μm in diameter (Plate 25).
3. Irregularly shaped black grains 10-150 μm in diameter (Plate 6).
4. Globular orange, red or brown grains 5-30 μm in diameter, occasionally exhibiting oolitic texture (Plate 24).

The above are individually interpreted as:-

1. colloidal, dominantly Fe oxides accumulating directly from the water column and preferentially adhering to the charged surfaces of clay minerals.
2. Incipient Fe-Mn micronodules, possibly resulting in part from diagenetic reactions involving the small-scale remobilisation of Mn.
3. Fe-Mn micronodules. The irregular shape of this material suggests that many of the micronodules represent fragments of detrital material coated with Fe-Mn oxides. This can be observed in cases where fragments of orange glass are only partially coated with black Fe-Mn oxides. This material is the most common form of ferromanganese material in the samples. Its abundance in these slowly accumulating sediments is entirely consistent with the suggestion that micronodules are more abundant under conditions of slow accumulation and/or reworking (e.g. Von Stackelberg 1979).

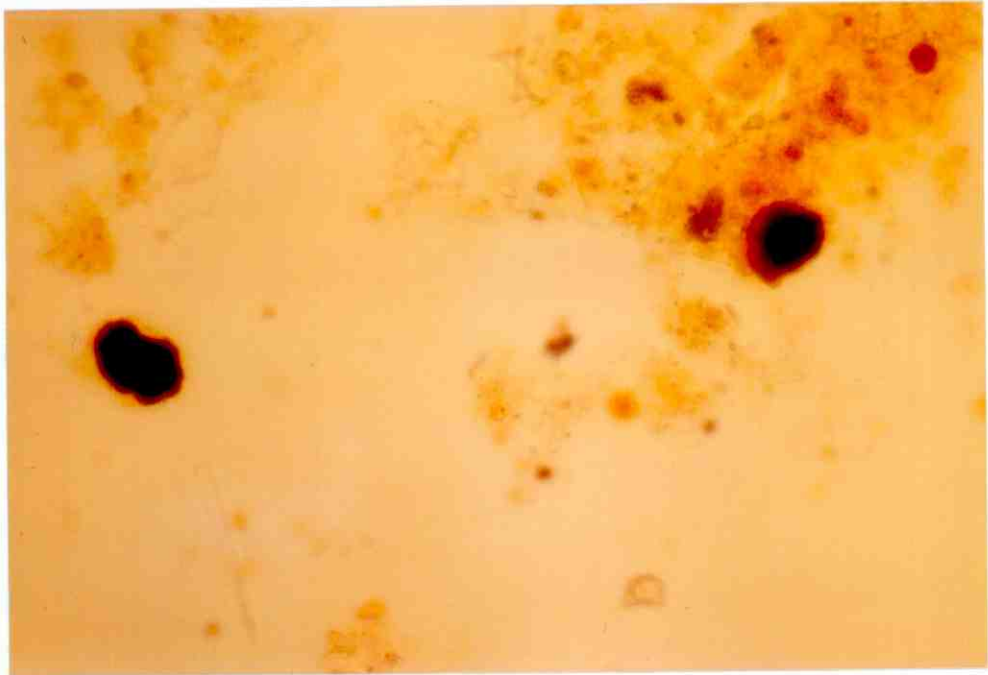


Plate 25. Photomicrograph of sediment sample K3-1,
showing ferromanganese micronodules. 1330 X.

4. Fe oxyhydroxides derived from the weathering of volcanic debris, mainly glass. This interpretation is based upon the predominance of this material in glass-rich samples, the advanced state of alteration of the glass and the orange colour of the most weathered material, since the colour of combined Fe-Mn oxides tends to be black. The globular or oolitic nature of the oxides (Plate 24) may result from the natural tendency of Fe oxyhydroxides to flocculate.

The absence of euhedral opaque minerals suggests that there is little or no magnetite or titanomagnetite in the sediments.

10.2.8 Quartz, feldspar and pyroxene

Whilst quartz and plagioclase feldspar are identified ubiquitously in bulk sediment X-ray diffractograms, their fine grain size in most sediments precludes smear-slide identification. Only in sediments from the Samoan Passage and the slopes of the Manihiki Plateau, which are proximal to volcanic sources, were recognizable feldspar grains up to 100 μm identified.

Pyroxene is much less common than feldspar. It does however, occur locally as grains up to 200 μm diameter (e.g. STYX 58, SOTW X 3FFA).

Again locally, mineral grains comprising several individual crystals of quartz and feldspar were observed, typically at diameters less than 150 μm .

10.2.9 Barite, rutile and authigenic feldspar

The authigenic Ti oxide mineral rutile was visually identified by smear slide in sample KK72-36, whilst barite was noted in KK72-32, KK72-35, M70-36 and STYXIV 10.

Ten to fifteen μm long laths of a low refractive index anisotropic mineral were seen in samples K1-5T and CATO 10. These are tentatively suggested to be crystals of authigenic feldspar, since detrital feldspar grains tend to be jagged and irregularly shaped.

10.3 Clay Mineralogy

10.3.1 Methods

Clay mineralogical determinations were made on 45 surface sediments and four sub-surface sediments. Whole sediments were disaggregated by ultrasound and wet-sieved to remove the coarse ($> 63 \mu\text{m}$) fraction. Weak ammonia solution was added to the slurry as a dispersant ($10 \text{ cm}^3 \text{ NH}_3 \cdot \text{H}_2\text{O}$ per litre) and the $< 2 \mu\text{m}$ fraction isolated by centrifugal settling.

Oriented mounts were made by vacuum filtration of weak clay suspensions onto ceramic disks. Cracking and/or curling of certain mounts, apparently related to the high proportion of smectite in the samples, could generally be overcome by redispersing the mounted material and repeating the vacuum filtration process.

Air-dried mounts were run on a Phillips X-ray powder diffractometer at $1^\circ 2\theta \text{ min}^{-1}$ between 2 and 60° , using $\text{CoK}\alpha$ radiation. To examine the swelling behaviour of the clays, glycerol treated mounts were run from 2 - $16^\circ 2\theta$. Mounts heated first to 400°C and then to 550°C were similarly run from 2 - $16^\circ 2\theta$, to examine the collapsing behaviour of the smectites, the possible occurrence of vermiculite and to differentiate kaolinite and chlorite. An example of the effect of each treatment on the resulting diffractograms is shown in Fig. 54.

With respect to other clay minerals, authigenic smectites are usually concentrated in the finer size fractions (i.e. $< 0.5 \mu\text{m}$). In an attempt to isolate smectites for chemical analysis, the $< 0.5 \mu\text{m}$ fraction of 9 sediments and 3 smectite-rich substrates of Fe-Mn crusts from the LIA were obtained by centrifugation. Only in one case did the resulting material consist only of smectite (Table 42), although in every case smectite was concentrated relative to its proportion in the $< 2 \mu\text{m}$ fraction.

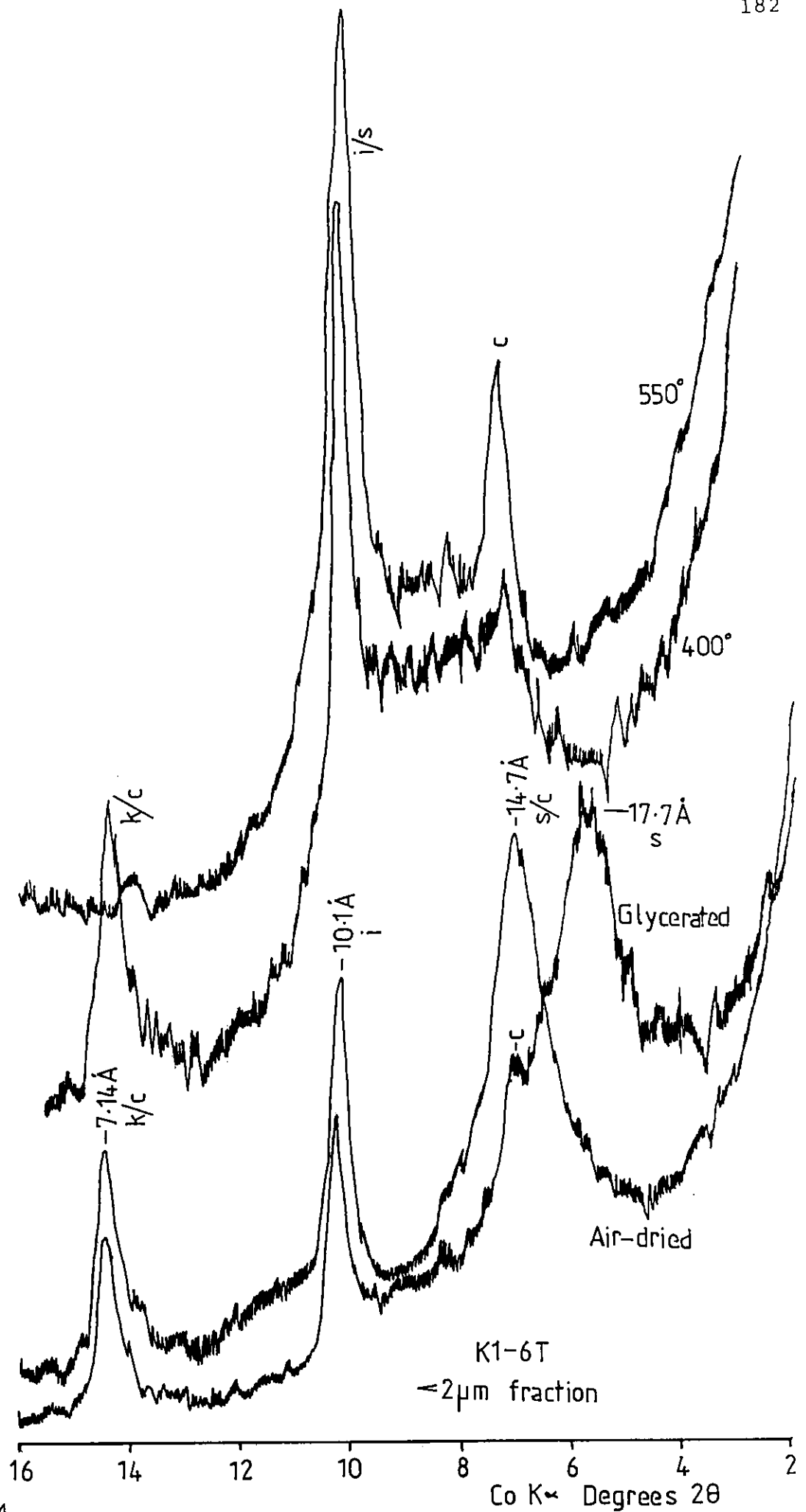


Fig.54

Low angle diffractograms of the $< 2\mu\text{m}$ fraction of sample K1-6T, showing the effect of treatments on the resulting trace. s=smectite, i=illite, k=kaolinite, c=chlorite.

Each $< 0.5 \mu\text{m}$ sample was treated with Morgan's solution (a pH5 mixture of sodium acetate and glacial acetic acid) to remove calcite, citrate-dithionite-bicarbonate to remove Fe oxides and oxyhydroxides (Mehra and Jackson 1960) and finally with 30% hydrogen peroxide to remove organic matter and Mn oxides. Filtration and washing through a $0.45 \mu\text{m}$ Nuclepore filter paper was performed between each leach. The long filtration time for these fine-grained fractions suggests a time-saving approach would be to chemically treat larger size fractions and to obtain the $< 0.5 \mu\text{m}$ fraction by centrifugation as a final step.

Major element analysis of the $< 0.5 \mu\text{m}$ fractions was performed by ICP following fusion with lithium metaborate (Appendix 3) and similarly for trace elements following dissolution by $\text{HF-HNO}_3\text{-HClO}_4$ (Appendix 3).

10.3.2 Distribution of the clay minerals

Semi-quantitative clay mineral percentages were calculated by Biscaye's (1965) method (Table 41). The peak area ratios of the maximum intensity X-ray reflections of all the clay minerals after glyceration are related to the corresponding weight ratios of clay minerals by known simple factors, i.e.

$$17\text{\AA} \text{ peak area} + 4 (10\text{\AA} \text{ peak area}) + 2 (7\text{\AA} \text{ peak area}) = \\ \% \text{ smectite} + \% \text{ illite} + \% (\text{kaolinite} + \text{chlorite})$$

The method assumes that the factors are invariant areally and that the sum of smectite + illite + kaolinite + chlorite accounts for the entire $< 2 \mu\text{m}$ fraction of the sediments. It is difficult to assess the accuracy of this method but it should be sufficiently precise to determine trends in the clay mineral distributions.

The regional distribution of clay minerals in the Pacific has been outlined, amongst others, by Griffin and Goldberg (1963) and Griffin et al. (1968). The present work shows good agreement with those results, which delineated the S. Pacific as a smectite-rich province.

Table 41 Semiquantitative clay mineral percentages calculated according to Biscaye's (1965) method.
Figures are rounded to 5%, and summed to 100%

Tokelau

Sample	SMECT.	ILLITE	KAO.+CHL.	Sample	SMECT.	ILLITE	KAO.+CHL.
K1-2T	60	25	15	M70-35	70	15	15
K1-2B	65	25	10	M70-36	70	25	5
K1-4T	50	35	15	CATO-10	65	25	10
K1-4B	70	20	10	CATO-28	65	25	10
K1-5T	50	30	20	CATO-32	55	30	15
K1-5B	65	25	10	SOTW-1A	55	30	15
K1-6T	50	35	15	SOTWX-2D	50	30	20
K1-6B	60	25	15	SOTWX-3A	50	35	15
S68-2	55	30	15	SOTWX-4B	55	35	10
M70-32	85	5	10	SOTWX-4C	50	30	20
M70-33	85	10	5	SOTWX-5A	50	35	15
M70-34	99	0	1	STYXIV-10	55	30	15
				STYXIV-12	45	40	15
				STYX 43	55	30	15

Penrhyn Basin

Sample	SMECT.	ILLITE	KAO.+CHL.	Sample	SMECT.	ILLITE	KAO.+CHL.
K2-1	55	30	15	C1-15	75	15	10
K2-1	80	10	10	C1-16	65	25	10
C1-3	65	25	10	C2-1	65	25	10
C1-4	65	20	15	M70-17	90	5	5
C1-7	70	20	10	STYX 35	70	20	10
C1-10	80	10	10	STYX 58	70	20	10
C1-13	85	10	5	STYX 66	75	15	10
				KK72-32	75	10	15

East Line Islands

Sample	SMECT.	ILLITE	KAO.+CHL.	Sample	SMECT.	ILLITE	KAO.+CHL.
K2-3	85	10	10	K2-14	80	10	10
K2-10	65	15	20	AMPH1A	75	15	10
K2-11	80	10	10	K3-1	85	10	5
K2-13	60	25	15	K3-2	85	10	5

Within the study area, the distribution of kaolinite + chlorite exhibits no regional trends, generally comprising 10-20% of the clay fraction. In contrast, smectite and illite show distinct and opposing trends (Figs. 55 + 56). From a minimum of approximately 50% in a N-S band centred on 169°W, smectite abundance increases both westwards and eastwards. In the Penrhyn Basin and to the east of the Line Islands there is a northwards increase in abundance, with smectite comprising 90% of the clay fraction in some sediments (Fig. 55).

Illite is greatest where smectite is least important, achieving abundances of 30-40% to the north of the Samoan Archipelago, declining eastwards to less than 10% of the clay fraction over large areas (Fig. 56).

The source of illite, kaolinite and chlorite is considered to be dominantly continental (Hein et al. 1979b + refs. therein). In contrast, deep-ocean smectite is formed mainly by authigenic processes. It is not an important constituent of atmospheric dust (Windom 1969) nor does it have an important riverine input (Hein et al. 1979b). By making the assumption that the input of continentally-derived clay minerals is constant in a region as remote from the continents as the S.W. equatorial Pacific, it may be inferred that variations in the relative proportions of the clay minerals are related to variations in the abundance of authigenic smectite.

10.3.3 Smectite mineralogy and chemistry

The smectite 001 X-ray reflections are generally broad but well defined, whilst higher order peaks are broader and much weaker (Fig. 54). Air-dried mounts gave smectite 001 peaks typically between 14.1 and 14.5Å, with a range of 13.7 - 15.1Å. Treatment with glycerol expanded the basal spacing to 17.7 - 18.3Å. Using the criteria of Reynolds and Hower (1970), there was no evidence of the presence of mixed-layered clays.

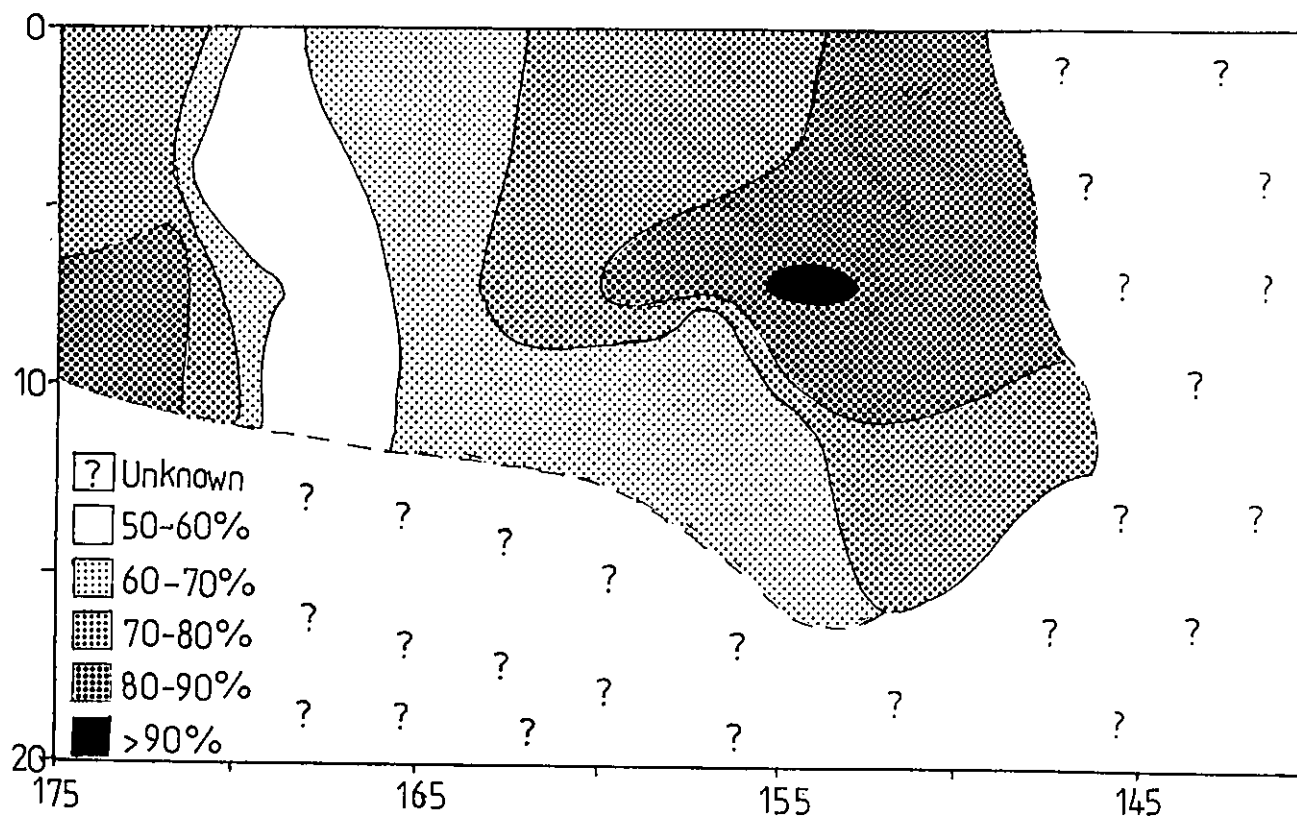


Fig.55 Distribution of smectite in the $<2\mu\text{m}$ fraction of surface sediments.

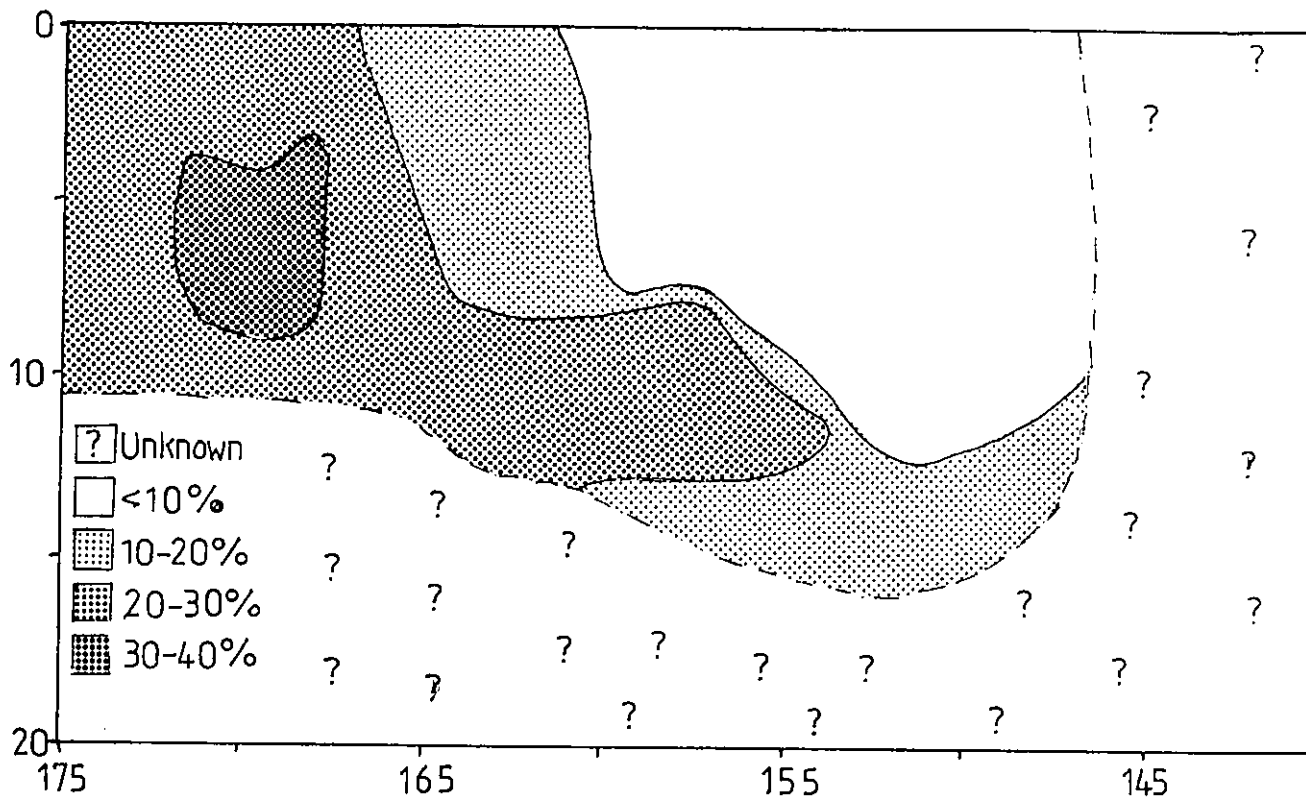


Fig.56 Distribution of illite in the $<2\mu\text{m}$ fraction of surface sediments.

There is little variation in the composition of the sediment $<0.5 \mu\text{m}$ fractions (Tables 42 + 43). Particularly, the Al_2O_3 , Fe_2O_3 and MgO contents are remarkably similar both within the S.W. Pacific samples and compared to the DOMES smectites (Table 42). The SiO_2 contents show more variation and exhibit a positive relationship with the abundance of biogenic silica in the sediments, probably reflecting the occurrence of biogenic silica in the $<0.5 \mu\text{m}$ fraction.

CaO and P_2O_5 contents are variable and strongly positively correlated. The P_2O_5 contents are very high, suggesting the probability of contamination by a Ca-P bearing phase. This is supported firstly by the identification of francolite in the $<0.5 \mu\text{m}$ fraction of substrate O60 2/4 and secondly by the occurrence of the highest Ca and P abundances in the $<0.5 \mu\text{m}$ fractions of sediments which are richest in phosphatic fish debris. Hein et al. (1979a) have observed fine grained apatite prisms in DOMES sediments, which they interpret as having formed by dissolution and reprecipitation of fish debris.

MnO , whilst a minor constituent, shows rather large variability and is most abundant in smectites occurring in Mn-rich sediments (Table 42). Hein et al. (1979b) have suggested that marine smectites may be interlayered with oxyhydroxides, a condition that could cause the exceptionally high layer charge of this type of smectite. The much lower layer charge of the S.W. Pacific smectites, well within the range quoted (0.2 - 0.6, Brindley 1980), does not however, argue against the presence of some Mn in the smectite lattice.

Substrate smectites, which are considered to be derived from the low temperature weathering of basaltic rubble, show a more variable chemistry than the sediment smectites. Although they are poorer in Mn and slightly depleted in Mg relative to the sediments, the range of most elements in the substrate smectites encompasses the composition of the sediment smectites and precludes certain differentiation between the two. For example, the high TiO_2 contents of the LI basalts (Jackson et al. 1976)

Table 42 Analyses of less than 0.5 μ m fractions. A:- Major oxides. Clay mineral percentages calculated according to Biscaye (1965)

<u>Sediments</u>	S	I	K+C	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Sum
K1-2B	75	13	12	46.13	12.62	8.82	4.01	1.28	2.66	1.62	0.88	0.84	0.16	79.02
M70-33	95	3	2	44.79	13.30	10.59	3.48	1.34	2.62	1.27	0.83	0.86	0.14	79.22
M70-34	98	1	1	49.26	11.98	7.65	3.65	0.95	1.51	0.97	0.48	0.33	0.13	76.91
SOTWX-4	77	14	9	40.78	12.14	7.54	3.73	2.06	1.78	1.44	0.92	0.97	0.09	71.45
C1-13	95	0	5	42.64	13.03	8.27	3.76	6.67	2.54	1.10	0.67	4.17	0.27	83.12
C1-15	86	9	5	41.70	13.89	9.35	3.46	5.61	1.62	1.35	0.82	3.45	0.28	81.53
K2-11	87	8	6	43.56	12.71	10.48	3.84	3.71	-	1.30	0.77	2.41	0.29	(79.07)
K3-1	90	4	6	45.94	13.15	8.81	3.88	3.35	2.34	0.89	0.60	2.29	0.20	81.45
STYX58	81	4	5	48.37	13.06	8.39	4.29	3.37	2.04	0.98	0.65	2.12	0.24	83.51
<u>Substrates</u>														
O51 2/7	95	2	2	42.87	6.94	17.21	3.48	0.67	2.04	2.68	2.29	0.48	0.05	78.71
O61 2/4	98	2	0	42.61	14.84	7.40	2.64	4.66	2.14	1.37	0.75	3.04	0.02	79.47
O63 8/9	100	0	0	44.80	14.35	12.15	2.57	0.15	2.24	2.61	0.98	0.15	0.05	80.05

Table 43 Analysis of less than 0.5 μ m fractions. B:- Trace elements

	← ppm →												
	S	I	K+C	Li	Sr	Ba	V	Cr	Co	Ni	Cu	Zn	Pb
<u>Sediments</u>													
K1-2B	75	13	12	48	131	520	97	85	22	70	460	220	100
M70-33	95	3	2	61	80	176	66	66	23	72	520	330	62
M70-34	98	1	1	36	80	320	85	186	26	117	580	770	103
SOTWX-4	77	14	9	41	93	390	100	43	20	66	470	320	85
C1-13	95	0	5	75	270	230	55	62	12	49	540	197	103
C1-15	86	9	5	56	240	260	69	63	19	66	550	230	137
K3-1	90	4	6	66	172	360	62	50	17	60	640	280	90
STYX 58	81	14	5	50	139	430	81	61	20	72	550	220	82
<u>Substrates</u>													
O51 2/7	95	2	2	42	33	103	46	64	27	99	460	390	46
O63 8/9	100	0	0	62	84	164	41	61	23	74	430	320	23

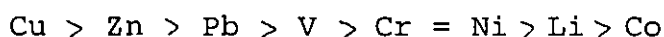
is not uniformly reflected in the smectites, two of which have Ti contents lying within the range of the sediment smectites.

The structural formulae of the more smectite-pure < 0.5 μm fractions were derived by the Ross and Hendricks (1945) method (Table 44). The Si/Al ratio in the tetrahedral layer is rather constant in both sediments and substrates, whilst the octahedral sites are filled predominantly with Al, Fe and Mg. In each case, the chemistry is indicative of a dioctahedral Fe-rich montmorillonite.

As would be expected in the marine environment, Na is the dominant inter-layer cation. Whilst some K occurs in the < 0.5 μm illite, there is overall a poor relation between illite and K. K is most abundant in the substrate smectite, in accordance with Melson and Thompson's (1973) observation that low temperature weathering of basalt yields K-rich smectites.

The layer charges of the smectites vary between 0.31 and 0.45 per half unit cell, well within the quoted range and similar to those calculated for Bauer Basin smectites, but much lower than those for DOMES smectites (Cole and Shaw in press, Hein et al. 1979b). Cole and Shaw (in press) have suggested that since deep-ocean sediments are metal-rich the high smectite layer charges reported by various workers may be due to the occurrence of trace metals in the lattice which are unaccounted for in their structural formulae. However, whilst generally rich in trace metals, the trace element contents of the S.W. Pacific (Table 43) and DOMES smectites are rather similar and invariant, with only Cu and Li being significantly greater in the high layer charge DOMES smectites.

Trace elements occur in abundances ranging from 20 ppm for Co to 500 - 600 ppm Cu. The following enrichment sequence is generally observed:-



Sr and Ba are not included in the list, since Sr correlates well with Ca and may substitute for it in apatite, and Ba may occur as fine-grained barite.

Table 44 Atomic properties of S.W. Pacific smectites

		M70-34	M70-33	C1-13	0512/7	0602/4	0638/9
Tetrahedral	Si	3.97	3.70	3.71	3.66	3.70	3.63
	Al	0.03	0.30	0.29	0.34	0.30	0.37
	Total	4.00	4.00	4.00	4.00	4.00	4.00
Octahedral	Al	1.10	0.99	1.07	0.38	1.21	0.99
	Fe	0.46	0.64	0.52	1.13	0.48	0.73
	Mg	0.44	0.42	0.47	0.44	0.34	0.31
	Ti	0.03	0.05	0.04	0.15	0.05	0.06
	Mn	0.01	0.01	0.02	0.004	0.02	0.01
	Total	2.04	2.11	2.13	2.10	2.09	2.19
Interlayer	Ca	0.16	0.24	-	0.12	-	0.02
	Na	0.24	0.42	0.43	0.42	0.36	0.35
	K	0.10	0.14	0.12	0.29	0.15	0.27
	Total	0.50	0.80	(0.55)	0.83	(0.51)	0.64
% smectite		98	95	95	95	98	100
illite		1	3	0	2	2	0
K + C		1	2	5	2	0	0
XS charge		-0.33	-0.45	-0.46	-0.32	-0.31	-0.33

10.3.4 Smectite formation

Cole and Shaw (in press) have summarized the mechanisms of smectite formation in the deep ocean into 3 general categories:-

1. The combination of hydrothermally derived silica and Fe oxide close to the point of debouchment of hydrothermal fluids into seawater (e.g. Bischoff 1972, Hekinian et al. 1978).
2. The low temperature weathering of basalt and basaltic debris both within the ocean basement and within sediments (e.g. Melson and Thompson 1973, Scheidegger and Stakes 1977, Kharin et al. 1979).
3. The combination of biogenic silica and Fe oxyhydroxides (Heath and Dymond 1977, Cole 1982).

The remarkably constant chemistry of the smectites argues against a diversity of origins throughout the region, and several strands of evidence argue for the combination of biogenic silica and Fe oxyhydroxide as the predominant mechanism of formation. Firstly, the compositions of the S.W. Pacific and the DOMES smectites are closely comparable (Table 45) and have Si/Al, Fe/Al, Mg/Al and Ti/Al ratios at the lower limit of the basaltic smectite range (Table 46). Secondly, there is an antipathetic relationship between regional volcanism, as denoted by the distribution of volcanic glass (Fig. 53), and smectite abundance (Fig. 55). Thirdly, there is parallel northwards increase in biogenic silica and smectite in the smectite-rich Penrhyn Basin and East Line Islands region.

Since the input of the continentally derived minerals kaolinite, chlorite and illite is assumed to be constant (Section 10.3.2), the greater abundance of smectite in the Penrhyn Basin and ELI sediments over the Tokelau sediments suggests that diagenesis is relatively more important in these slowly accumulating sediments, even in surface samples where there is no biogenic silica present. In such sediments the siliceous skeletal material which reaches the seabed (see Honjo 1978) must be entirely consumed at the sediment-water interface.

Table 45 Composition of some smectites formed in the marine environment

Formation Mechanism	Reference	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO
1	Bischoff (1972)	48.0	0.02	36.7	2.39	0.69	1.60	2.10	-	0.26
	Hekinian et al. (1978)	49.35	0.52	30.38	2.37	0.05	-	2.27	0.03	0.14
2	Melson + Thompson (1973)	48.4	15.9	15.2	10.7	0.6	1.0	2.4	0.4	0
		50.0	12.3	12.7	11.7	0.8	1.0	3.0	2.0	0.06
	Scheidegger + Stakes (1977)	44.81	6.67	14.9	14.98	2.09	1.98	1.21	0.34	-
	Kharin (1979)	46.14	13.85	9.59	16.21	1.13	2.85	1.12	1.75	0.17
3	Dymond + Eklund (1978)	52.3	2.44	29.7	6.10	0.48	0.61	2.04	0.03	0.77
	Hein et al. (1979)	45.69	14.1	9.24	5.21	0.88	2.78	2.24	0.65	0.43
	This work:-									
	M70-33	44.79	13.30	10.59	3.48	1.34	2.62	1.27	0.83	0.14
	K3-1	45.94	13.15	8.81	3.88	3.35	2.34	0.89	0.60	0.20
	O63 8/9	44.80	14.35	12.15	2.57	0.15	2.24	2.61	0.98	0.05

- 1 Hydrothermal
- 2 Low temperature weathering of basalt
- 3 Combination of biogenic silica and Fe oxyhydroxide

Table 46 Ranges of element ratios in sediment and substrate smectites, and of smectites from weathered basalts. Also data from Domes and Bauer Basin smectite. Data from Table 42 & 45.

<u>Ranges of element ratios</u>					
	$\frac{\text{Si}}{\text{Al}}$	$\frac{\text{Fe}}{\text{Al}}$	$\frac{\text{Mg}}{\text{Al}}$	$\frac{\text{Ti}}{\text{Al}}$	$\frac{\text{Mn}}{\text{Al}}$
Sediments	2.65-3.63	0.82-1.09	0.28-0.36	0.05-0.09	0.01-0.03
Substrates	2.53-5.46	0.66-3.28	0.20-0.57	0.06-0.37	0.003-0.01
Weathered Basalts	2.34-5.84	0.56-3.12	0.42-2.10	0.03-0.38	0.- 0.02
DOMES	2.86	0.87	0.42	0.05	0.04
Bauer	18.9	16.1	2.84	0.01	0.47

Since Mn does not easily enter the smectite lattice (Eklund 1974), a consequence of the biogenic silica - Fe oxyhydroxide reaction is to fractionate Mn from Fe between oxide + silicate phases (Lyle et al. 1977). The observation that Penrhyn Basin + EPI sediments have higher Mn/Fe ratios in the oxide phases in comparison to the Tokelau sediments is consistent with the greater importance of the combination reaction in those sediments (see Section 11.5.2.8).

Because two of the three substrate smectites, which are presumed to be derived dominantly from basalt alteration, have very similar compositions to the sediment smectites, a volcanic source cannot be ruled out for at least some of the smectite. Authigenic clays have been observed developing on volcanic debris (Plate 21). However, it may be that the alteration process is too slow to be of importance in surface sediments. Hein and Scholl (1978) have shown that it takes between 3 and 5 My for andesitic ash beds to alter to smectite, although fine volcanic dust may alter quicker. At the slow sedimentation rate of 0.5 mm ky^{-1} , this still represents 1.5-3 metres of sediment. Further work, including the examination of the REE patterns of the smectites (Bonnot-Courtois 1980) and their Rb/Sr isotopic composition (Hoffert et al. 1978), would help to resolve the problem.

The suggestion that much of the smectite in the S.W. Pacific is formed by the combination of biogenic silica and Fe oxyhydroxide is contrary to the mainstream of opinion which considers it to be volcanically derived. For example, Griffin et al. (1968) have pointed to the general abundance

of volcanic glass, phillipsite and smectite in S. Pacific sediments and have suggested that the glass is the precursor of phillipsite and smectite. The present work indicates that the distribution of phillipsite and smectite is similar in the S.W. equatorial Pacific but is not related to that of glass. Rather, both phillipsite and smectite appear to be authigenic minerals which can nucleate and develop in the absence of volcanic glass, possibly as a response to the dissolution of siliceous microfossils.

The compositional similarity of the S.W. equatorial Pacific and N.E. equatorial Pacific smectites is striking, particularly in view of the greater abundance of biogenic silica in the latter in comparison to the more metal-rich former. One explanation for this would be that the specified reaction of set stoichiometry occurs at the surface of the microfossil between biogenic silica and a trace metal bearing oxide phase which away from hydrothermal regions has a rather constant Fe: Al ratio. Close to hydrothermal sources, the Fe:Al ratio is larger, which is reflected in the greater Fe:Al ratios in resulting smectites.

Chapter 11 Sediment Geochemistry

11.1 Introduction

Deep-sea sediments are mechanical mixtures of several components which may be classified according to their source as biogenic, terrigenous, volcanic, hydrogenous and hydrothermal ('metalliferous') (Bischoff et al. 1979). Variations in the chemical composition of the sediments reflect differences in the supply of each fraction coupled with chemical changes which occur within the sediments (Heath and Dymond 1977, Bischoff et al. 1979, Dymond 1981).

As a constituent of the sediment, it may be expected that the chemistry of Fe-Mn nodules might similarly reflect processes of element supply and sediment diagenesis. Particularly, since nodules are composed dominantly of hydrogenous material, comparison of their composition with the hydrogenous fraction of sediments may represent the most promising approach to elucidating sediment-nodule inter-relationships. However, previous attempts at relating nodule chemistry to the composition of bulk sediments or individual sedimentary phases have met only with limited success (Calvert et al. 1978, Piper et al. 1979, Skornyakova 1979, Stoffers et al. 1981).

The dual purpose of this chapter, therefore, is to examine the controls on sediment geochemistry in the S.W. equatorial Pacific and to ascertain inter-relationships between sediment and nodule composition. Attention is focused on the hydrogenous components of the sediments and nodules.

11.2 Techniques

25 surface sediments and four from 50 cm depth were collected by free-fall grab and gravity corer during the 1980 CCOP/SOPAC cruises, and 47 surface sediments were obtained from existing cores from the University of Hawaii, Scripps Institution of Oceanography and Lamont

Doherty Geological Observatory. Nodules, either at the core top or in the free-fall grabs, were found associated with 39 of the sediments. Sample locations are shown in Fig. 57.

Sediments were dried over silica gel at room temperature and finely ground in an agate pestle and mortar. Ten elements (Mn, Fe, Cu, Ni, Co, Pb, Zn, Ca, Al and Ti) were determined by atomic absorption spectrophotometry (AAS) on a Perkin-Elmer 5000 spectrophotometer with a deuterium background correction facility. Bulk data is given in Appendix 4. Levels of accuracy, determined through the analysis of in-house standards were generally better than 8%, and precisions better than 5% (see Appendix 3). In carbonate-rich sediments, the precision for Pb declined as levels fell towards the detection limit.

Since CaCO_3 can generally be regarded as a diluent, compositional data used here are on a CaCO_3 -free basis, calculated using the formula of Dymond et al. (1976). In this the CaCO_3 content of a sediment is determined by partitioning the Ca content of the sediment into seasalt, noncarbonate and carbonate fractions. Representative samples were leached with deionised water to determine salt contents and analyses made of acetic acid - leached residues to determine the non-carbonate Ca contents. It should be borne in mind that uncertainties in the resulting data are introduced in cases where the CaCO_3 content is low, due to variability in the non-carbonate Ca values, and in relatively pure carbonate sediments for which high correction factors are applied. Further, sediments rich in biogenic silica (e.g. M70-34) do not benefit from the procedure. In the present suite of sediments, however, biogenic silica rarely exceeds 15% of the bulk sediment, and many sediments are from below the CCD (Chapter 10).

To isolate the hydrogenous phase, each sample was leached with hydroxylamine hydrochloride-acetic acid (HHA, Chester and Hughes 1967, see Appendix 3 for method)

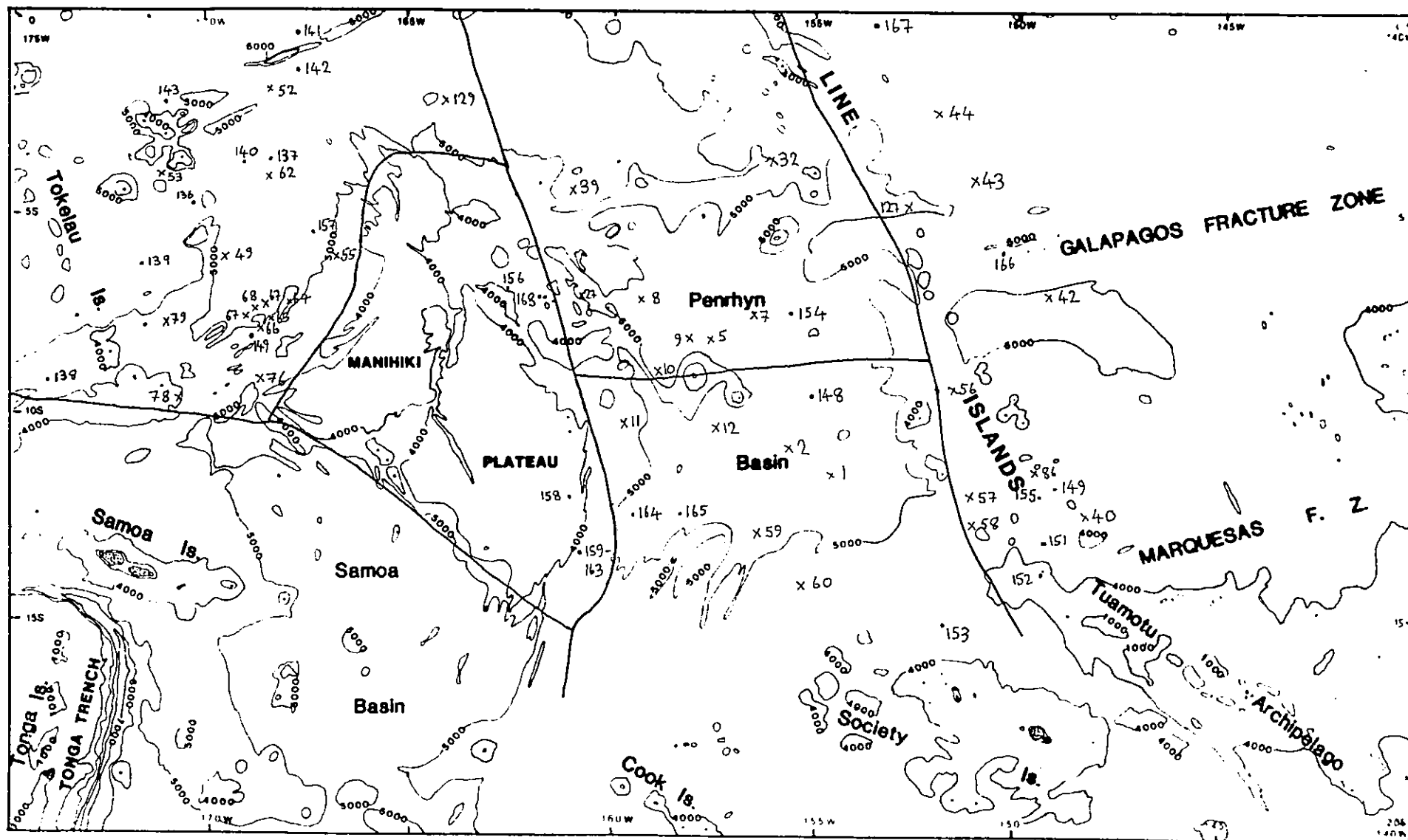


Fig.57 Sediment sample locations. Sites at which nodules were also obtained are marked with an 'x'. Numbers refer to stations listed in Appendix 4.

and the leachate analysed by AAS for the standard 10 element suite. Whilst a lack of similarly leached samples precludes a determination of accuracy, precision was generally better than 10%. Analyses of selected residues were made, the sum of residue plus leachate being in agreement with the bulk composition, within the limits of precision.

HHA is considered to leach CaCO_3 and adsorbed ions plus Mn oxides and amorphous Fe and Mn oxides from marine sediment. To obtain a fuller picture of the hydrogenous sediment fraction, selected samples were leached with ammonium oxalate - oxalic acid buffered to pH3 (Appendix 3 for method). Oxalate does not leach crystalline Fe oxide phases (Landa + Gast 1973). Analysis of the leachates was performed by AAS, and precision was better than 10% for most elements.

11.3 Major oxides

For purposes of comparison with previous work, data for the major elements Mn, Fe, Al and Ti are reported as oxides.

To facilitate identification of regional trends, the data were divided into three areas; first, the area to the west of the Manihiki Plateau, comprising the Samoan Passage and the western Central Pacific Basin (Tokelau region); second, the Penrhyn Basin; and third, the area to the east of the Line Islands Archipelago (ELI, Fig. 57).

The mean compositions of the three areas, with comparative data for 'average Pacific pelagic clay' (Ppc) and for DOMES area B in the N.E. equatorial Pacific (Bischoff et al. 1979) are given in Table 47.

Leaching with HHA indicates that 80-85% of the Fe, 90% of the Al and 98% of the Ti in the sediments occur in the non-hydrogenous phases (Table 48). Away from hydrothermal areas, Al is usually assigned to the clay hydrolysate fraction, and can be used to normalise other elements to this fraction (Heath and Dymond 1977). The good correlation between Fe and Al ($r = 0.74$, Fig. 58)

Table 47 Average bulk chemical compositions of sediments from the S.W. Equatorial Pacific, Pacific pelagic clay and other Pacific regions. (Numbers in parentheses are one standard deviation). Oxides in % bulk sediment. Elements in ppm

	Tokelau (CaCO ₃ -free)	Penrhyn (CaCO ₃ -free)	ELI (CaCO ₃ -free)	DOMES B ¹	Tiki ² (CaCO ₃ -free)	Bauer ³ (CaCO ₃ -free)	Ppc ¹
Al ₂ O ₃	11.5(2.5)	11.4(1.4)	10.9(1.7)	12.5	10.7(1.4)	6.1(1)	16.6
Fe ₂ O ₃	8.4(2.4)	8.9(2.4)	8.2(2.5)	5.4(0.8)	22.3(6.1)	22.6(5.0)	7.7
CaO	-	-	-	1.5(0.6)	-	-	0.7
TiO ₂	1.4(0.5)	1.0(0.7)	0.66(3.6)	0.95(0.28)	-	-	0.78
MnO	0.96(0.37)	2.0(0.6)	2.5(1.0)	0.53(0.4)	5.37(0.54)	7.4(1.6)	0.56
Co	93	197(48)	221(70)	62(27)	263(74)	-	113
Cu	281(139)	446(115)	467(109)	222(70)	390(136)	1170(220)	230
Ni	245(342)	338(102)	434(187)	112(66)	682(161)	1070(260)	210
Pb	48(28)	70(17)	48(25)	26(8)	83(51)	-	34
Zn	143(31)	167(77)	176(56)	95(13)	159(79)	410(50)	165

¹ Data from Bischoff et al. (1979)

² Data from Hoffert et al. (1979)

³ Data from Heath and Dymond (1977)

Table 48 Percentage of each element leached from
sediments by hydroxylamine hydrochloride -
acetic acid

	Tokelau			Penrhyn		
	Mean	S.D.	Range	Mean	S.D.	Range
Mn	82	15	27-100	91	11	39-100
Fe	15	4	7-24	21	6	3-30
Cu	48	16	17-66	52	12	26-73
Ni	50	18	7-90	74	17	19-100
Co	71	15	20-100	74	18	10-100
Pb	67	22	11-100	66	22	35-100
Zn	50	13	31-100	40	14	17-66
Al	8	3	2-14	6	3	3-20
Ti	2	4	0.3-21	2	3	0.1-12

suggests that Fe is significantly associated with this phase.

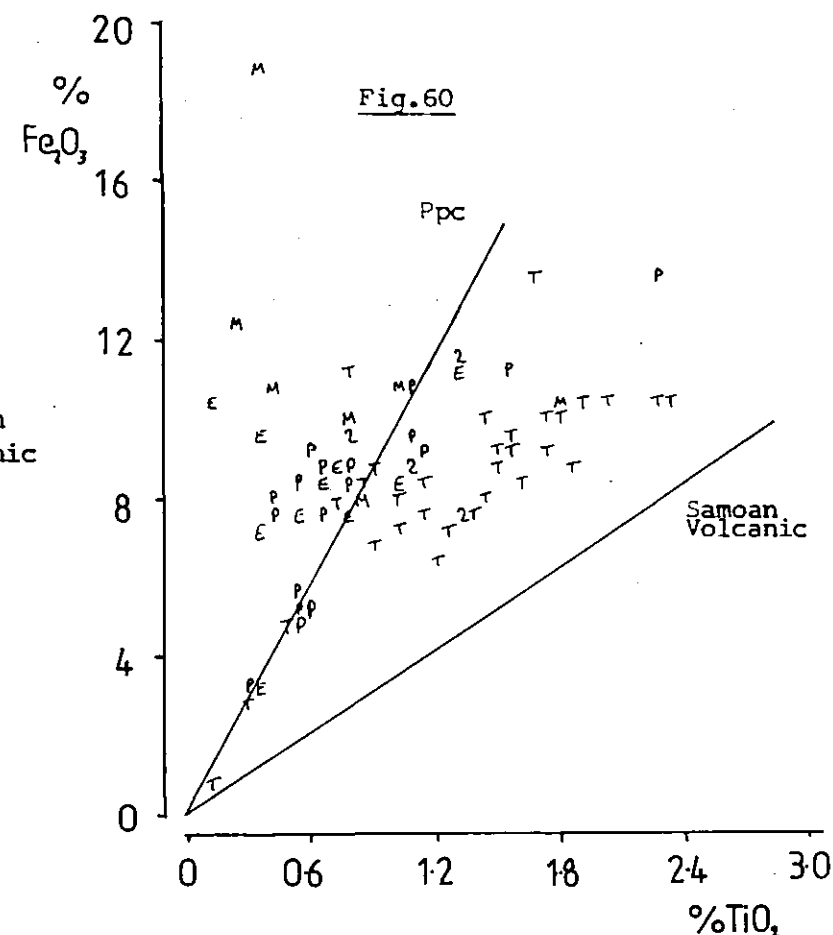
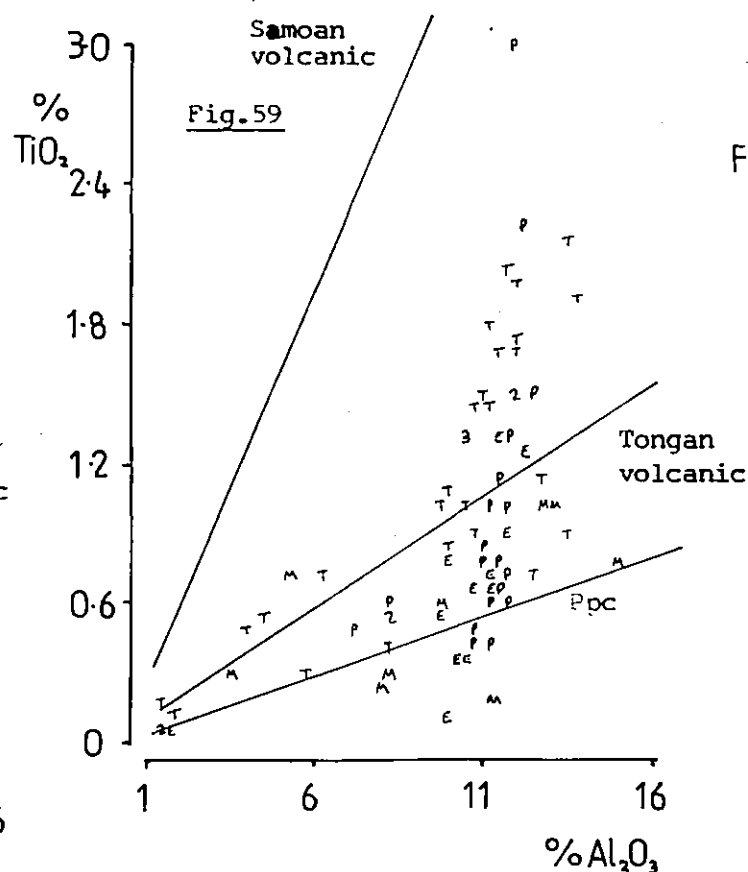
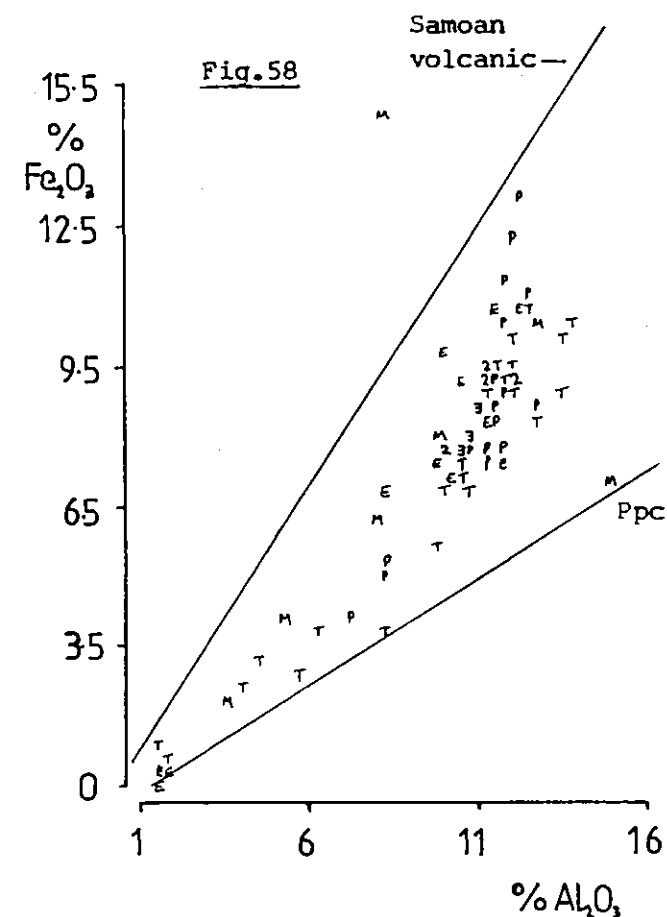
Fe is enriched over Al relative to Ppc in the study region. This is interpreted as being due to the greater than average volcanic influence in the region compared to terrigenous influence (Fe/Al continental crust = 0.68, Fe/Al basalt = 0.98, Krauskopf 1967). Sediments with particularly high Fe_2O_3 contents generally contain relatively high abundances of volcanic glass (V18-278, V18-284, C1-1, V18-280, V18-281).

There is a rather poor relationship between Ti and Al ($r = 0.50$, Fig. 59). The S.W. Pacific sediments are generally Ti rich compared to Ppc and DOMES B sediments and exhibit a west-east decrease from a maximum of 2.4% TiO_2 (CaCO_3 free) in the Samoan Passage to 0.5% to the east of the LI (Fig. 62). The distribution of TiO_2 closely resembles that of volcanic glass (Fig. 53) inferring a source of Ti-rich volcanic material in the west of the region. The most likely source is the Samoan Archipelago (Chapter 10).

Although there is a poor relation overall between Fe_2O_3 and TiO_2 (Fig. 60), reflecting differential partitioning between authigenic, volcanic and clay hydrolysate phases, the Fe_2O_3 and TiO_2 contents of Tokelau sediments are quite well defined by the mixing line of Ppc and Samoan volcanic material (Fig. 61). In the Penrhyn and ELI areas, where volcanism is a less important influence (Chapter 10), Fe is likely to be dominantly within the clay mineral phases, since Fe rich montmorillonite is the predominant clay mineral in the region (Section 10.3).

High TiO_2 contents are also seen in the S.E. Penrhyn Basin close to the Society Islands (Fig. 62), which have been volcanically active within the last 2 My (Dymond 1975).

By their high abundance of volcanic glass, the sediments which show the greatest volcanic influence are those from the edge of the Manihiki Plateau (Fig. 53). Despite this, their TiO_2 contents are generally less than 1%, which is



Figs. 58-60 Plots of Fe₂O₃ vs. Al₂O₃, TiO₂ vs. Al₂O₃ and Fe₂O₃ vs. TiO₂ for sediment samples from the Tokelau region (T), the Manihiki Plateau (M), the Penrhyn Basin (P), and the East Line Islands (E). Where 2 or more overlap, the number designates the number of coincident samples. Ppc is average Pacific pelagic clay (data from Bischoff et al. 1979). Data for Samoan volcanic is taken from Natland (1980). Data for Tongan volcanic is taken from Ewart et al. (1977).

due to the TiO_2 -poor nature of the Manihiki volcanism, (Jackson et al., 1976).

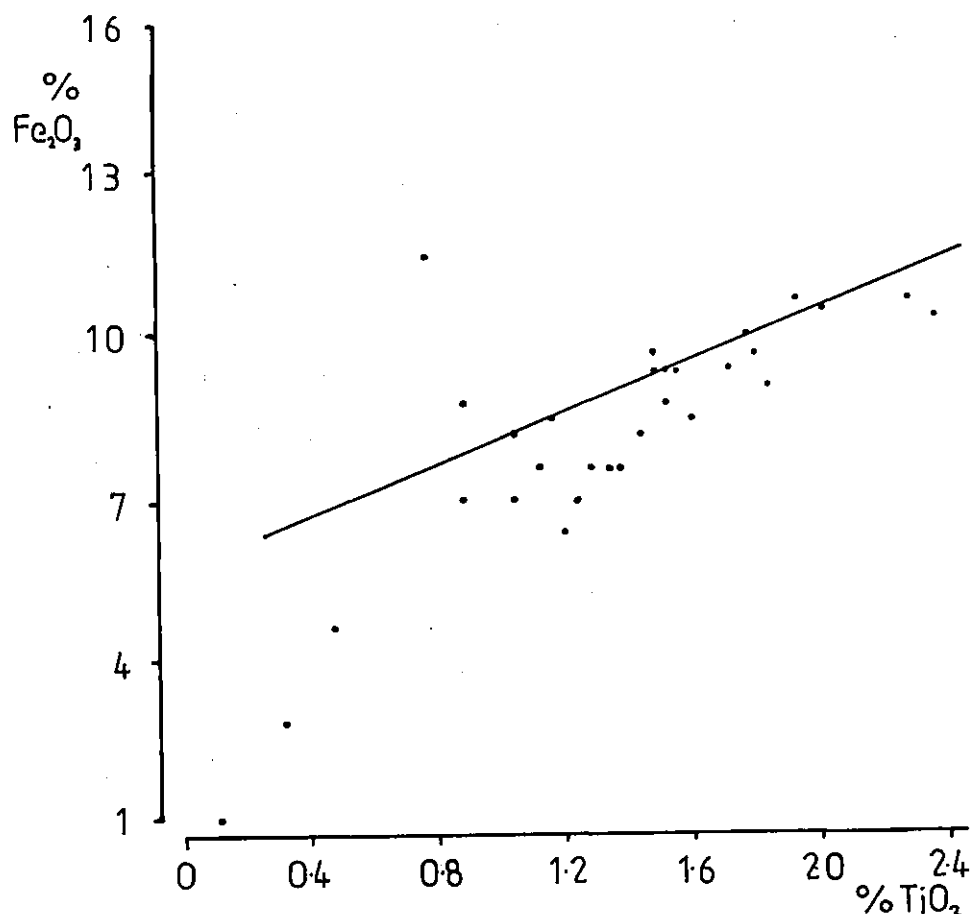


Fig. 61 Plot of Fe_2O_3 versus TiO_2 for the Tokelau sediments, with the mixing line of Ppc and Samoan basalt.

The plots of MnO versus Al_2O_3 and Fe_2O_3 (Figs. 63 and 64) show that Mn is enriched throughout the region compared to Ppc and the DOMES area. Ratios of $\text{MnO}/\text{Al}_2\text{O}_3$ and $\text{MnO}/\text{Fe}_2\text{O}_3$ (Table 49) increase from west to east reflecting the increase in the MnO content of the sediments (Fig. 65). Particularly, MnO is enriched in the Penrhyn and ELI sediments with respect to the Tokelau sediments.

Sediments from the Tiki Basin, to the east of the study area at $10^\circ - 18^\circ\text{S}$, $130^\circ - 140^\circ\text{W}$ are metal-rich and have compositions similar to those from the Bauer Deep (Hoffert et al. 1979, see Table 47) which have been

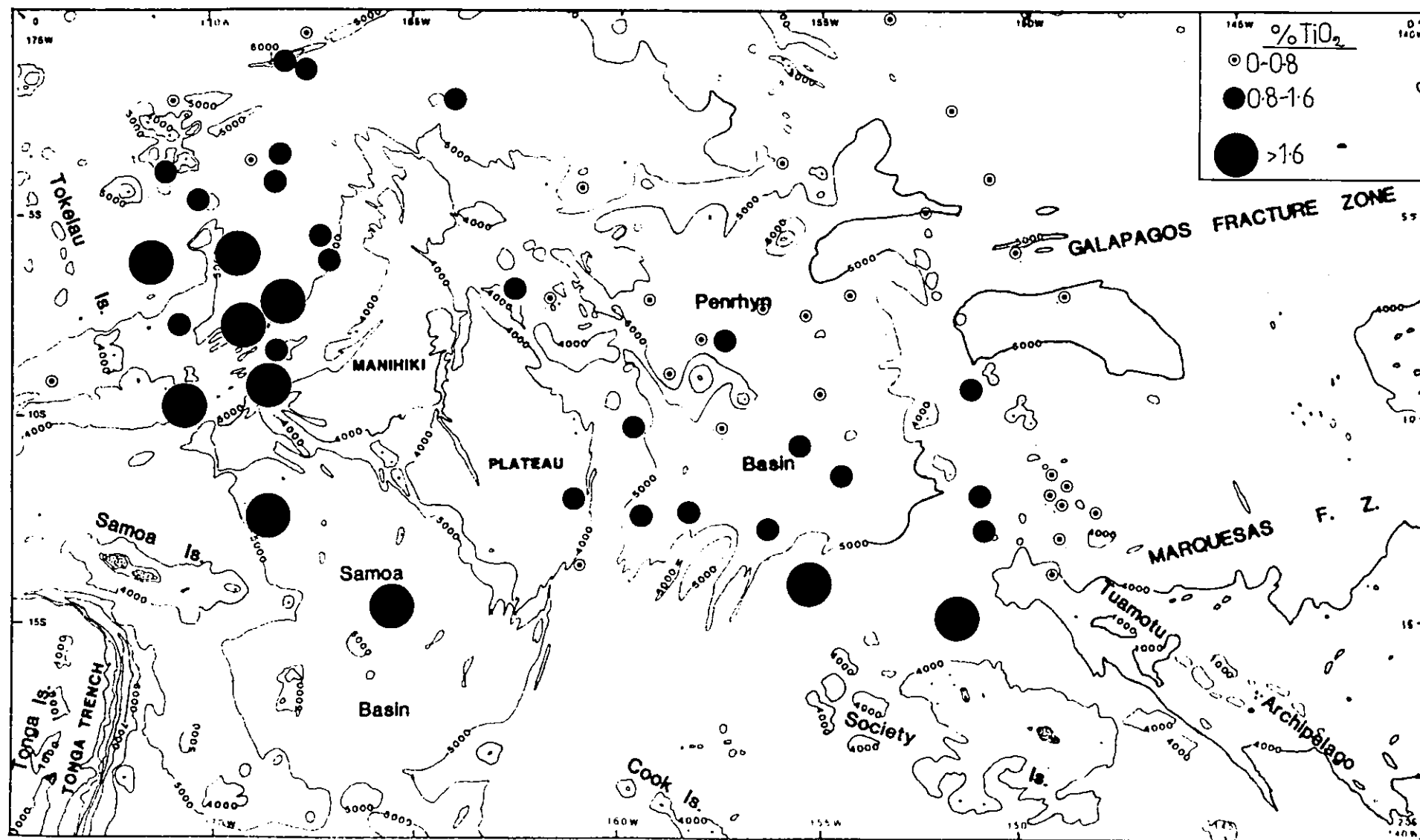
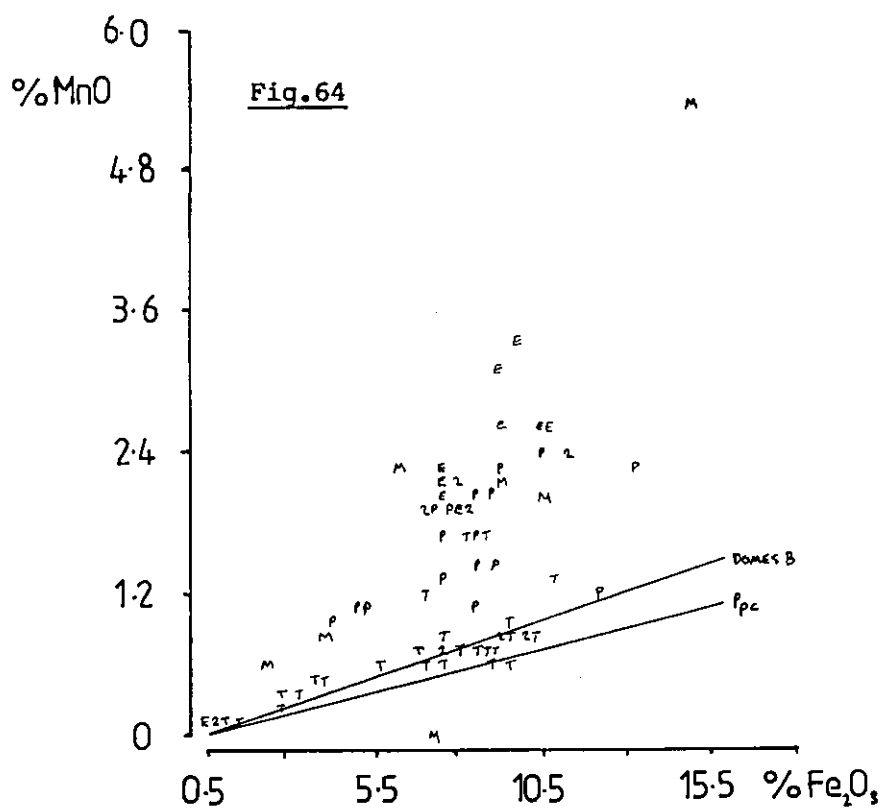
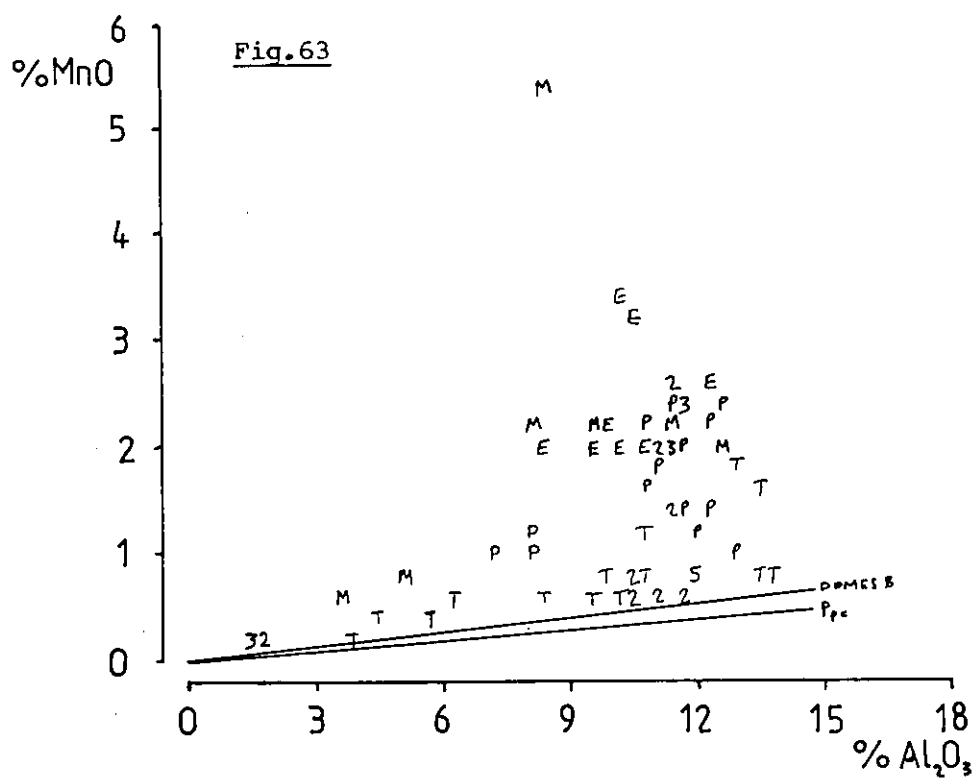


Fig.62 Distribution of TiO_2 in surface sediments (CaCO_3 -free basis).



Figs.63+64 MnO vs. Al₂O₃ and Fe₂O₃ in surface sediments. Symbols as in Fig.58. Data for DOMES B region from Bischoff et al. (19

interpreted as containing an important hydrothermal component (Heath and Dymond 1977). The Tiki Basin is situated at the latitude at which there is a strong westerly mid-depth circulation (Reid 1981) which disperses hydrothermal effluent derived from the East Pacific Rise (Edmond et al. 1982). Plotting the Tiki sediments on the Al-Fe-Mn triangular diagram of Dymond et al. (1976) (Fig. 67) reveals the similarity of the Tiki and Bauer sediments, supporting the idea of a direct hydrothermal influence in that region.

In contrast, there is no evidence for such influence further west. The sediments have much lower MnO and Fe₂O₃ contents, and exhibit much lower Fe₂O₃/Al₂O₃ and MnO/Al₂O₃ ratios than the Tiki sediments. Further they plot close to the 'Pacific sediments' field on Fig. 67, and adjacent to the basaltic end-member on Boström's (1973) diagram of mixing curves of 'East Pacific Rise metalliferous sediment' and basaltic or terrigenous debris (Fig. 66).

Since approximately 90% of the Mn is within the HHA-leachable phases, it is concluded that the Mn is accumulating slowly in the oxide form directly from the water column. Assuming the accumulation rate of hydrogenous material to be relatively constant through time, the Mn content of the sediments should be inversely proportional to the sedimentation rate of other phases (Krishnaswami 1976). This is strongly supported by the close correspondence of the Mn distribution (Fig. 65) and the distribution of indicators of slow sedimentation - fish debris (Fig. 51), phillipsite (Fig. 52) and authigenic calcite, feldspar and rutile (see Chapter 10).

There is a west-east increase in MnO/Fe₂O₃ which parallels that in MnO/Al₂O₃, the MnO/Fe₂O₃ ratio of the Penrhyn and ELI sediments being very similar to that of the hydrothermally-influenced Tiki sediments (Table 49). Away from the immediate vicinity of hydrothermal vents, where differential rates of oxidation of Mn and Fe fractionates these elements (Bignell et al. 1976), the ratio of Mn to Fe is a poor indicator of hydrothermalism,

Table 49 Selected oxide & elemental ratios for averaged S.W. Equatorial Pacific sediments,
Pacific pelagic clay and other Pacific regional sediments. Calculated from Table 47

	Tokelau	Penrhyn	ELI	DOMES B	Tiki	Bauer	Ppc	HHA	LI
$\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$	0.72 (0.10)	0.77 (0.13)	0.73 (0.17)	0.43	2.1	3.7	0.46		
$\text{TiO}_2/\text{Al}_2\text{O}_3$	0.11 (0.03)	0.09 (0.05)	0.06 (0.03)	0.05	0.09	-	0.05		
$\text{MnO}/\text{Al}_2\text{O}_3$	0.074 (0.02)	0.16 (0.04)	0.20 (0.07)	0.04	0.50	1.2	0.033		
$\text{MnO}/\text{Fe}_2\text{O}_3$	0.11 (0.034)	0.21 (0.04)	0.26 (0.05)	0.10	0.24	0.33	0.07		
Co/Mn	0.014 (0.002)	0.014 (0.001)	0.014 (0.003)	0.015	0.006	-	0.026	0.012	0.025
Cu/Mn	0.043 (0.012)	0.03 (0.008)	0.03 (0.02)	0.054	0.009	0.020	0.053	0.021	0.009
Ni/Mn	0.033 (0.030)	0.025 (0.006)	0.03 (0.01)	0.027	0.016	0.019	0.048	0.020	0.020
Pb/Mn	0.008 (0.003)	0.005 (0.002)	0.002 (0.001)	0.006	0.002	-	0.008	0.004	0.005
Zn/Mn	0.032 (0.028)	0.014 (0.010)	0.014 (0.010)	0.023	0.004	0.007	0.038	0.020	0.003
Cu/Ni	1.15	1.32	1.08	1.98	0.57	1.09	1.10		

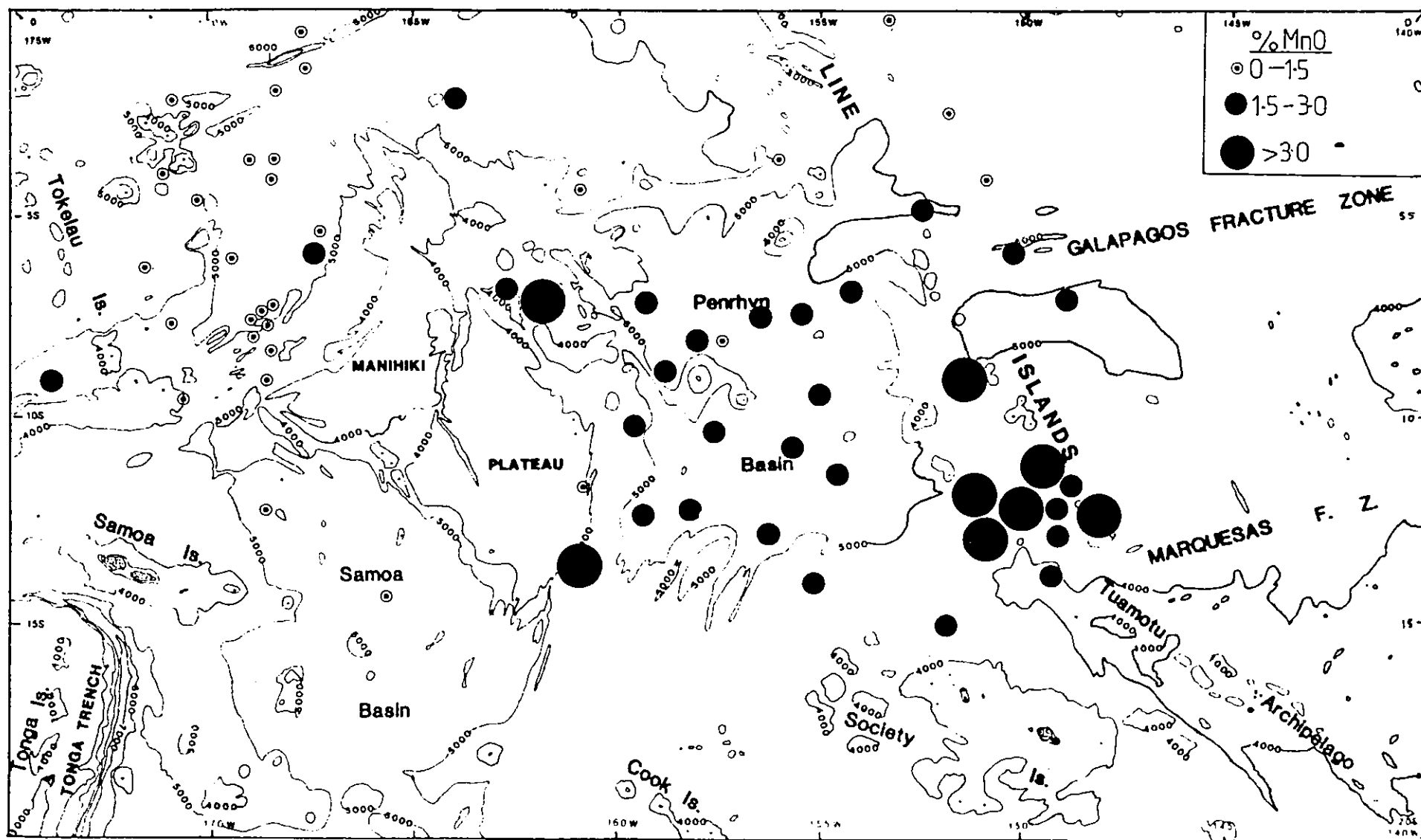


Fig.65 Distribution of MnO in surface sediments. (CaCO_3 -free basis)

since mixing and scavenging processes obscure the original relationships. Better indicators are the $\text{MnO}/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratios, which are much greater in the Tiki and Bauer sediments than in the Tokelau or Penrhyn sediments.

Krishnaswami (1976) has observed an inverse relation between the Mn content and sedimentation rate in some Pacific cores, which he interprets as being due to a constant supply of hydrogenous material superimposed upon a variable sedimentation rate. In the previous chapter it was shown that sedimentation rates are exceptionally low in the Penrhyn Basin and ELI region, lower than in the Tokelau region, the DOMES region (Quinterno and Theyer 1979) and by definition lower than the average Ppc. The eastwardly increasing $\text{MnO}/\text{Fe}_2\text{O}_3$ and $\text{MnO}/\text{Al}_2\text{O}_3$ ratios, which are higher than in Ppc or DOMES sediment, are interpreted as being due to a greater proportion of hydrogenous material ($\text{Mn}/\text{Fe} \approx 1$, $\text{Mn}/\text{Al} > 1$) in a mechanical mixture of it and detrital phases ($\text{Mn}/\text{Fe} \approx 0.02$, $\text{Mn}/\text{Al} 0.02$, Krauskopf 1967) in the Penrhyn Basin and ELI region.

11.4 Trace elements

The correlation coefficients for CaCO_3 -free element data (Table 51) suggests that to a greater or lesser extent Co, Cu, Ni and Pb are associated with Mn, and thus the hydrogenous phase. Zn is also an important constituent of the hydrogenous phase (Table 48) but exhibits a weak correlation with Mn, both in the total data set and when the data is areally divided. This may in part be due to the inclusion of data from sediments derived from Zn-contaminated cores, from the University of Hawaii, despite a careful vetting procedure.

Plots of Cu, Ni, Co, Pb and Zn versus Mn (Figs. 68-72) bear out the generality that the elements are important constituents of the hydrogenous phase. As the hydrogenous content of the Penrhyn and ELI sediments is greater than that of the Tokelau sediments, so are their Ni, Co, Cu, Pb and Zn contents (Table 47).

Table 50 Correlation coefficients of elemental concentrations of bulk sediment. Values underlined are significant at the 0.001 level N= 75

Significant at 0.001 at $r = 0.37$

	Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb
Fe	<u>0.66</u>								
Ca	<u>-0.43</u>	<u>-0.73</u>							
Al	<u>0.45</u>	<u>0.85</u>	<u>-0.86</u>						
Ti	<u>0.07</u>	<u>0.60</u>	<u>-0.51</u>	<u>0.60</u>					
Cu	<u>0.87</u>	<u>0.67</u>	<u>-0.54</u>	<u>0.56</u>	0.06				
Ni	<u>0.84</u>	<u>0.52</u>	<u>-0.34</u>	<u>0.38</u>	-0.04	<u>0.85</u>			
Co	<u>0.91</u>	<u>0.63</u>	<u>-0.53</u>	<u>0.54</u>	0.17	<u>0.81</u>	<u>0.71</u>		
Pb	<u>0.67</u>	<u>0.62</u>	<u>-0.61</u>	<u>0.57</u>	0.31	<u>0.60</u>	<u>0.42</u>	<u>0.75</u>	
Zn	<u>0.70</u>	<u>0.81</u>	<u>-0.80</u>	<u>0.77</u>	<u>0.44</u>	<u>0.72</u>	<u>0.63</u>	<u>0.69</u>	<u>0.60</u>

Table 51 Correlation coefficients of carbonate-free elemental concentrations. Values underlined are significant at the 0.001 level N = 75

Significant at 0.001 at $r = 0.37$

	Mn	Fe	Al	Ti	Cu	Ni	Co	Pb
Fe	<u>0.62</u>							
Al	0.27	<u>0.74</u>						
Ti	-0.29	<u>0.45</u>	<u>0.50</u>					
Cu	<u>0.85</u>	<u>0.51</u>	0.29	<u>-0.40</u>				
Ni	<u>0.69</u>	<u>0.53</u>	0.30	-0.25	<u>0.69</u>			
Co	<u>0.86</u>	0.45	0.32	-0.27	<u>0.71</u>	<u>0.52</u>		
Pb	<u>0.47</u>	<u>0.50</u>	0.34	0.05	0.31	<u>0.50</u>	<u>0.48</u>	
Zn	<u>0.47</u>	<u>0.52</u>	<u>0.37</u>	0.27	<u>0.38</u>	<u>0.42</u>	<u>0.41</u>	0.13

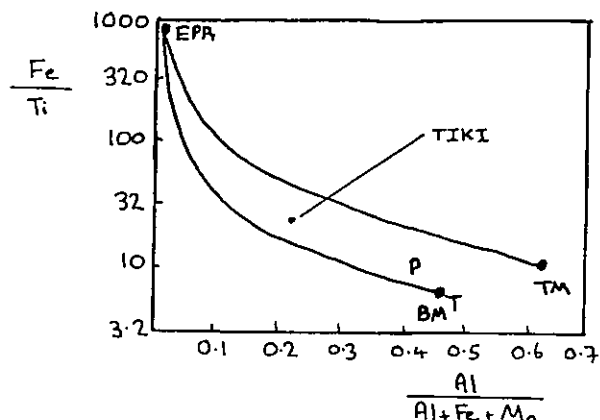


Fig. 66 Fe/Ti vs. Al/(Al+Fe+Mn) (after Bostrom 1973) showing compositional relationship of sediment from the Penrhyn Basin (P), the Tokelau region (T) and the Tiki Basin (Hoffert et al. 1979) to terrigenous matter (TM), basaltic debris (BM) and metalliferous sediment from the EPR.

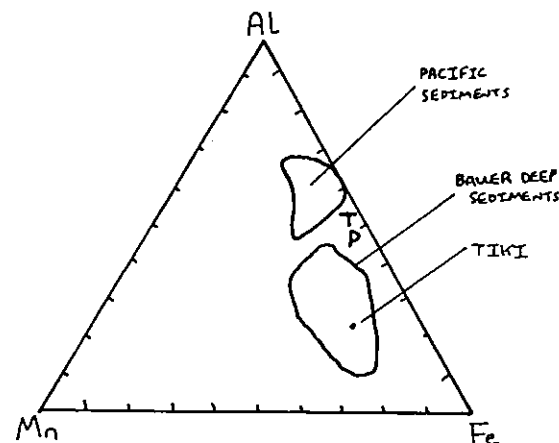
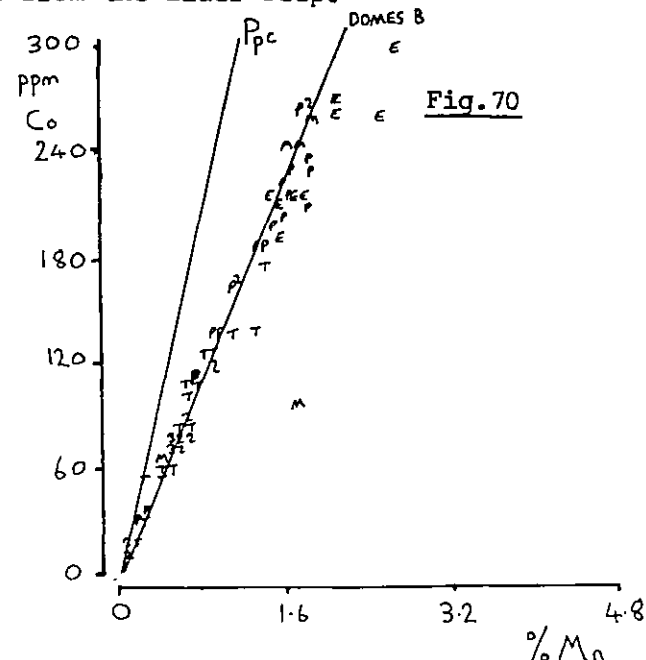
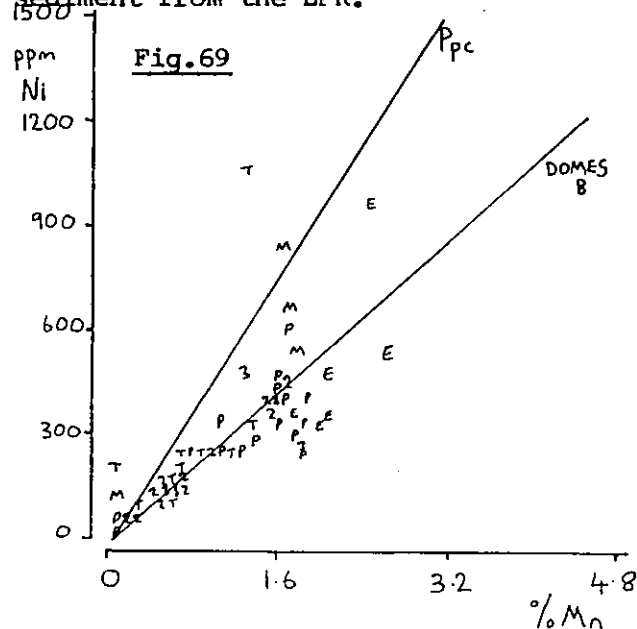
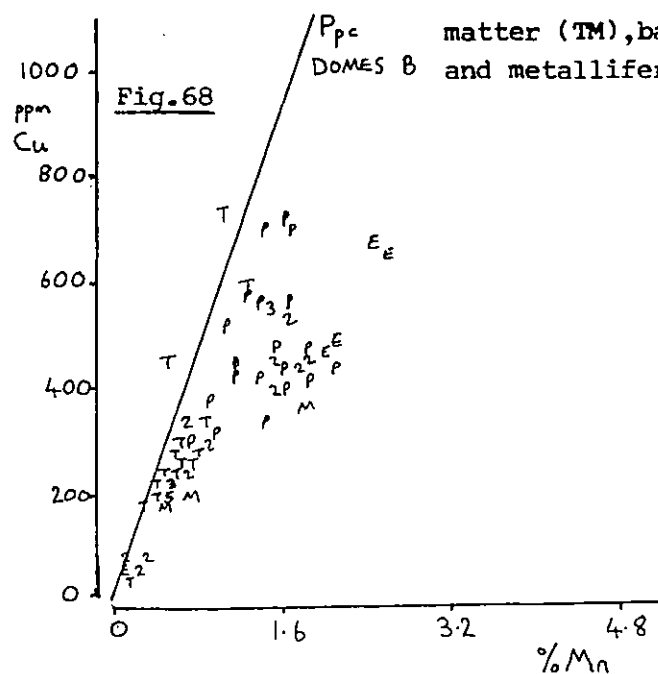
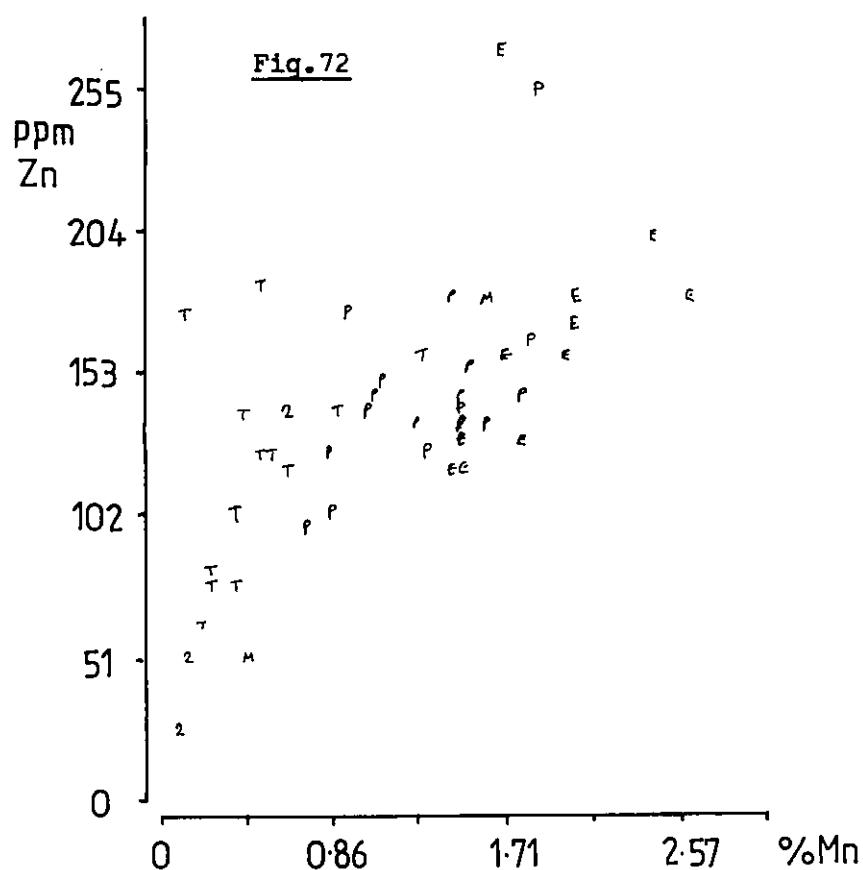
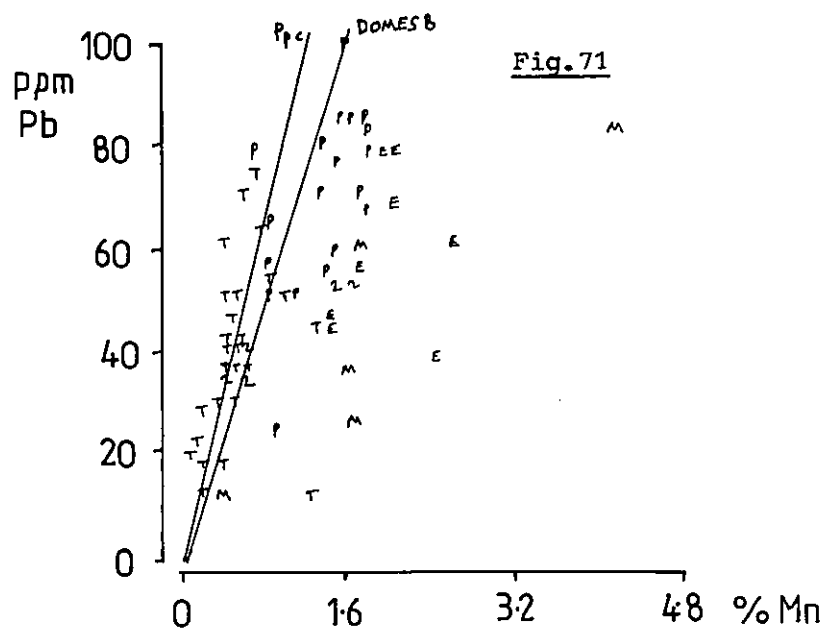


Fig. 67 Al-Fe-Mn triangular diagram (after Dymond et al. 1976) relating sediment composition of sediments from the Penrhyn Basin (P), Tokelau region (T) and the Tiki Basin to Pacific pelagic sediments and metalliferous sediments from the Bauer Deep.



Figs. 68-70 Cu, Ni and Co vs. Mn in surface sediments from the S.W. equatorial Pacific. Symbols as in Figs. 58+63.



Figs. 71+72 Pb, Zn vs. Mn in surface sediments from the S.W. equatorial Pacific. Symbols as in Figs. 58+63.

When comparing sediments from different regions, which are likely to contain different proportions of sedimentary components and which may have been analysed using differing procedures, it is often more instructive to examine element ratios than absolute element abundances (Table 49).

Variability in element ratios may be caused by variations in the supply of one element relative to another, variable diagenetic behaviour or by a non-uniform partitioning of the elements between each sediment component. In the absence of reliable element supply data, the former hypothesis is difficult to test. One may note that the Cu/Mn ratio of the Bauer sediments is twice that of the Tiki sediments. Simple scavenging processes might be expected to yield higher element/Mn ratios in Tiki sediments, since the Tiku Basin is located at a greater distance from the presumed Mn source at the EPR. For Cu, therefore, alternative supply processes are likely. The close association of Cu with organic material (Irving and Williams 1953, Sunda and Hanson 1979), the greater productivity of surface waters in the eastern Pacific compared to the central Pacific (Koblentz-Mishke et al. 1970) and the high Cu/Mn ratios of faecal material (Chapter 9) all suggest that Cu is supplied to the sediment-water interface in association with organic material and is scavenged by Mn oxides within the sediment. The Cu/Mn ratios in the study area are lower than in the DOMES area, reflecting the lower productivity in the SWP, but greater than the Bauer and Tiki sediments, where a hydrothermal supply of Mn is inferred.

The data suggests that the converse may be true for Co and that scavenging within the water column is an important control. The Tiki sediments have a much lower Co/Mn ratio than the S.W. Pacific or DOMES sediments, which have essentially identical Co/Mn ratios. Both Co and Mn occur dominantly in the hydrogenous phase, and their ratio therefore reflects the composition of that phase. Since there is no evidence for a hydrothermal source for Co, it is possible that the adsorption of Co

onto Mn oxide is a time-dependent process occurring in the water column. Tiki Mn oxides, ponded from the EPR, may have spent relatively little time in the water column and are thus Co-depleted.

The data for Ni (Fig. 69) suggests that it is behaving more similarly to Co than to Cu, in contrast to Zn, (Fig. 72), which appears to be more closely related to Cu.

Variability in element ratios may also be caused by heterogeneous partitioning between sediment phases. As a greater proportion of the total Mn occurs in hydrogenous phases in comparison to other trace elements, element/Mn ratios in the insoluble sediment fraction are correspondingly greater. An increasing hydrogenous influence will therefore tend to reduce the element/Mn ratios on a total sediment basis, which is seen in the S.W. Pacific for Cu/Mn and Pb/Mn.

The high cation exchange capacity of smectite and its dominance in the regional clay mineral assemblage suggests that it may be an important control on some trace metals. Analyses of smectites isolated from S.W. Pacific sediments (Table 42) show that typical trace metal contents are:- Cu 500 ppm, Zn 250 ppm, Pb 100 ppm, Ni 70 ppm and Co 20 ppm. By assuming a sediment clay content of 30%, and that 70% of the Penrhyn clay is smectite (50% in the Tokelau region, Fig. 55), it can be calculated that 25-30% of the total Cu, 30-35% Pb, 20-40% Zn, 5% Ni and 3% of the total Co is contained in the smectite phase. A significant proportion of the non-hydrogenous Cu, Pb and Zn rests in smectite, whilst most non-hydrogenous Ni and Co is within other phases. Although only 50% of the total Cu is hydrogenous, the Mn-Cu correlation is enhanced by the observed correlation between smectite content and Mn content of the sediments (Figs. 55 and 65).

11.5 Partition geochemistry

Each sediment sample was leached with hydroxylamine hydrochloride-acetic acid (HHA), which removes amorphous metal oxides, CaCO_3 and weakly adsorbed ions (Chester and Hughes 1967; see Appendix 3 for method). Levels of Mn, Fe, Ca, Al, Ti, Cu, Ni, Co, Pb and Zn in the leachate were determined by AAS. Mean levels of precision for Mn, Fe, Cu, Ni, Ca and Al were better than 10%, declining to 14% for Pb, 29% for Co and 37% for Ti.

In addition, selected samples were leached with a pH3 mixture of 0.2M ammonium oxalate and 0.2M oxalic acid (AOOA; Schwertmann 1964). As for HHA, the AOOA leach removes amorphous oxyhydroxides but does not attack crystalline Fe oxides (Landa and Gast 1973) or Fe-rich smectite (Heath and Dymond 1977). Element determinations on the leachates were made by AAS. Precision was better than 5% for Mn, Fe, Cu, Ni, Co and Al and 9% for Ti, but was only 27% for Zn, 49% for Pb and 69% for Ca.

11.5.1 Insoluble sediment fraction (ISF)

Residues of fourteen HHA sediments were analysed by AAS following dissolution in $\text{HF-HNO}_3\text{-HClO}_4$.

Relative to shale, the ISF is somewhat depleted in MnO , Al_2O_3 and CaO but is enriched in Fe_2O_3 and TiO_2 (Table 52). Normalisation of the major oxides to Al_2O_3 allows compositional comparisons to be made between areas (Table 53). Tables 52 and 53 indicate that whilst the DOMES area ISF is rather similar in composition to terrigenous shale, the S.W. Pacific sediments have higher but more variable $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CaO}/\text{Al}_2\text{O}_3$ and $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios, suggestive of a mixture of terrigenous material with a locally important volcanic component. In addition, the high abundance of Fe-rich montmorillonite in the sediments (Section 10.3) will also increase the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratios.

Table 52 Average composition of the HHA insoluble sediment fraction of fourteen sediments from the S.W. equatorial Pacific. Analysis by AAS. Also shown are values for shale (Turekian and Wedepohl 1961) and DOMES B (Piper et al. 1979). Oxides in weight %, elements in ppm. Figures in parentheses represent standard deviations (range for DOMES B)

Oxide/ Element	S.W. Pacific	DOMES	Shale
MnO	0.052 (0.012)	0.054 (0.004)	0.11
Fe ₂ O ₃	8.73 (1.93)	6.42 (0.46)	6.75
Al ₂ O ₃	12.61 (1.70)	13.64 (0.93)	15.15
TiO ₂	1.04 (0.40)	0.75 (0.05)	0.77
CaO	1.64 (1.35)	0.68 (0.08)	3.09
Cu	250 (120)	-	45
Ni	50 (10)	-	68
Co	12 (3)	17.8 (0.8)	19
Pb	7 (9)	-	20
Zn	100 (20)	165 (12)	95

Table 53 Major oxide ratios of the sediment fraction insoluble in HHA. Mean (and standard deviation) of 14 sediments; data for shale (Turekian + Wedepohl 1961), Samoan basalt (Natland 1981) and DOMES B (Piper et al. 1979) included for comparison

	S.W. Pacific	DOMES	Shale	Samoan Basalt
MnO/Al ₂ O ₃	0.004 (7 x 10 ⁻⁴)	0.004	0.007	0.017
Fe ₂ O ₃ /Al ₂ O ₃	0.689 (0.117)	0.471	0.446	1.17
CaO/Al ₂ O ₃	0.144 (0.132)	0.050	0.205	0.91
TiO ₂ /Al ₂ O ₃	0.082 (0.025)	0.055	0.051	0.32

The trace metal contents of the ISF are similar to those of shale and the DOMES area ISF, except for Cu, which is enriched five-fold over shale. This is almost certainly caused by its high concentration (400 ppm) in the smectite.

11.5.2 Hydroxylamine hydrochloride - acetic acid soluble sediment fraction (HSF)

The HSF consists of amorphous metal oxides, both in dispersed form and as micronodules and coatings, CaCO_3 , seasalt and adsorbed ions. Subtraction of the sedimentary CaCO_3 content from the total percentage of the sediment leached by HHA gives a measure of the hydrogenous plus seasalt content of the sediment. Most sediments in the S.W. Pacific give values of 10-20%, ranging from 2-28% (Appendix 4). Half of this may be seasalt. In comparison, DOMES surface sediments generally contain less than 10% hydrogenous material plus seasalt (Piper et al. 1979). Since the SWP sediments are accumulating less rapidly than the NEP sediments (Chester and Aston 1976, Quinterno and Theyer 1979), these findings are consistent with the trace element veil model of metal accumulation (Wedepohl 1960), in which sediment composition is considered in terms of a constant rain of hydrogenous material superimposed upon a variable accumulation rate of lithogenic and biogenic material (Krishnaswami 1976).

11.5.2.1 Composition of the HSF

The proportion of each element which is leachable by HHA (Table 54) signifies that Mn, Co and Pb are contained dominantly within the hydrogenous fraction, that Fe, Al and Ti are dominantly within the non-hydrogenous fraction and that Cu, Ni and Zn are partitioned in similar proportions between the two. In addition, a regional analysis (Table 54) shows that a larger fraction (99% confidence level) of the Mn, Fe and Ni is leached from Penrhyn sediments than from Tokelau sediments, and vice versa for Zn and possibly Al. Leachable Ti, Co and Pb are similar throughout.

Table 54 Mean percentage of elements leachable by HHA in Penrhyn Basin and Tokelau sediments expressed as a % of the total metal content. Values in parentheses represent one standard deviation. Student's t test is for differences between the percentage of each element leached in each area

	Tokelau	Penrhyn	t (t _{0.01} = 2.65)
Mn	82(15)	91(11)	-3.0
Fe	15 (4)	21 (6)	-6.0
Cu	48(16)	52(12)	-1.3
Ni	50(18)	74(17)	-6.0
Co	71(15)	74(18)	-0.75
Pb	67(22)	66(22)	0.2
Zn	50(13)	40(14)	4.5
Al	8 (3)	6 (3)	2.9
Ti	2 (4)	2 (3)	0
N	30	36	

11.5.2.2 Element associations

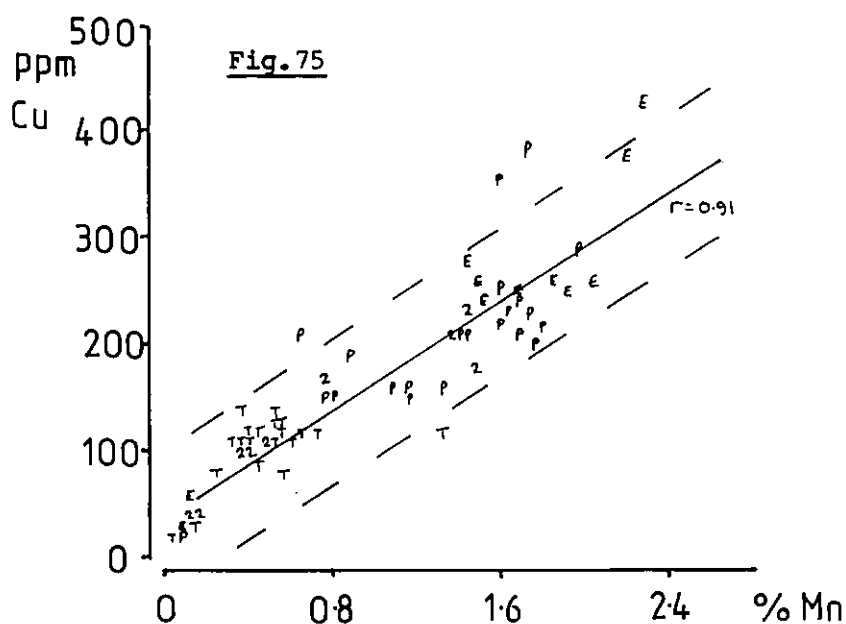
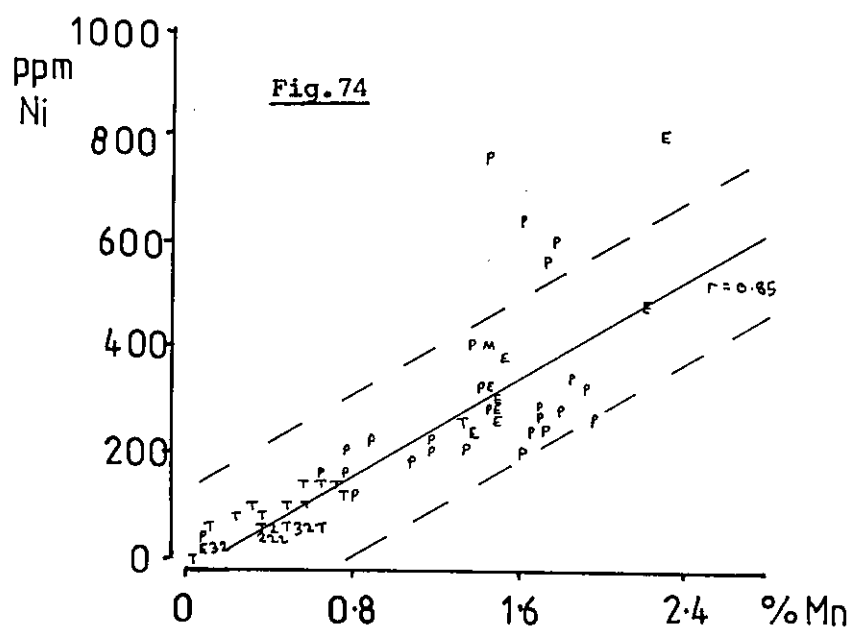
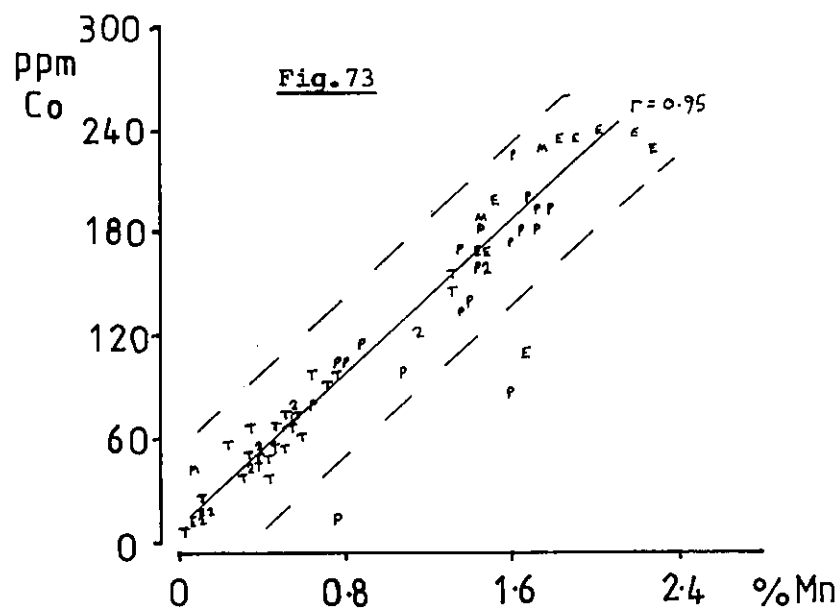
The rather high correlation coefficient between Mn and Fe in the HSF ($r = 0.74$, Table 55) reflects to a large extent the variable proportion of hydrogenous material in a suite of sediments with widely different sedimentation rates. Since CaCO_3 is a major sediment builder (Hays et al. 1969), this may be shown by removing carbonate rich ($>30\% \text{CaCO}_3$) sediments from the data set, which results in a reduction in the Mn-Fe coefficient to 0.48 for the Penrhyn sediments and 0.04 for the Tokelau sediments. Piper et al. (1979) found no correlation between Mn and Fe in DOMES sediment.

Co, Ni and Cu all correlate more strongly with Mn than with Fe (Table 55, Figs. 73-75). In contrast, Zn appears to be related to neither Mn nor Fe (Fig. 76). This is at variance with results from the DOMES area, where a strong Zn:Mn correlation was observed (Piper et al. 1979).

Table 55 Correlation matrix of sediment fraction soluble in hydroxylamine hydrochloride
- acetic acid. Values underlined are significant at the 0.001 level.

N = 72 significant at 0.001 at $r = 0.38$

	Mn	Fe	Cu	Ni	Co	Pb	Zn	Al	Ti
Fe	<u>0.74</u>								
Cu	<u>0.91</u>	<u>0.65</u>							
Ni	<u>0.85</u>	0.36	<u>0.87</u>						
Co	<u>0.95</u>	<u>0.76</u>	<u>0.83</u>	<u>0.78</u>					
Pb	<u>0.68</u>	<u>0.77</u>	<u>0.56</u>	0.37	<u>0.70</u>				
Zn	0.05	0.14	0.14	0.11	0.10	0.10			
Al	0.02	<u>0.37</u>	0.14	-0.10	0.06	0.30	0.26		
Ti	-0.11	-0.08	-0.11	-0.09	-0.18	-0.21	-0.21	-0.26	
Mn/Fe	<u>0.66</u>	0.06	<u>0.57</u>	<u>0.78</u>	<u>0.59</u>	0.32	0.00	-0.28	-0.26



Figs. 73-75 Co, Ni, Cu vs. Mn in the hydroxylamine hydrochloride-acetic acid soluble sediment fraction (HSF). Each element is expressed in ppm or weight of the bulk sediment. r represent the linear correlation coefficient between the element and Mn in the HSF. See also Fig. 79.

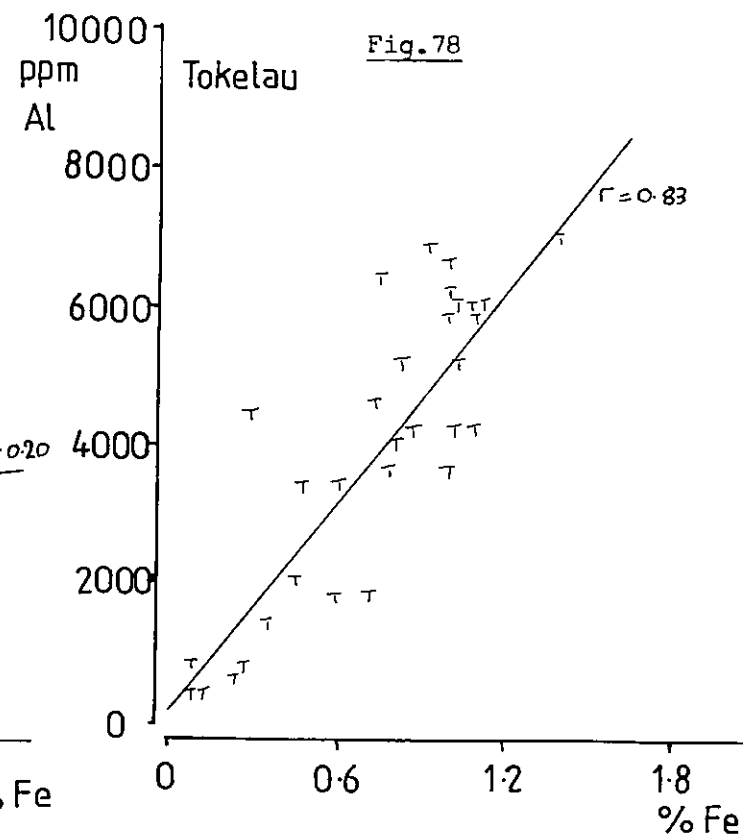
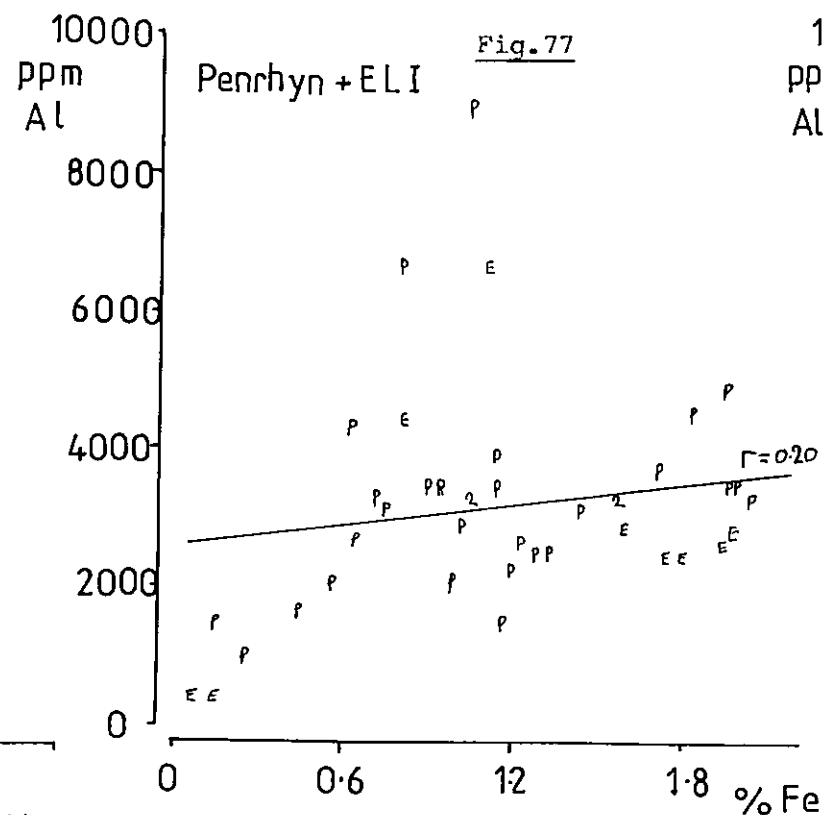
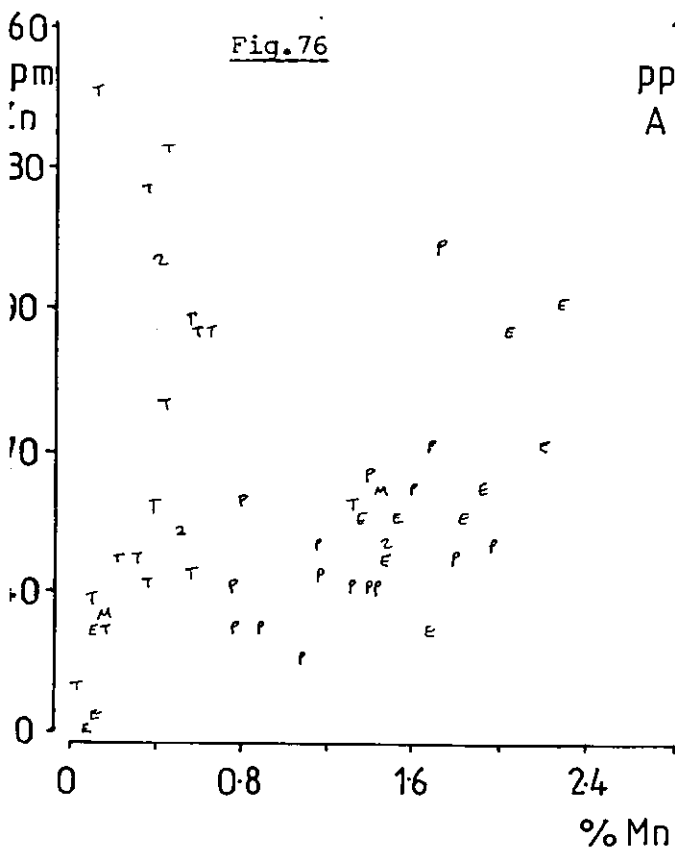
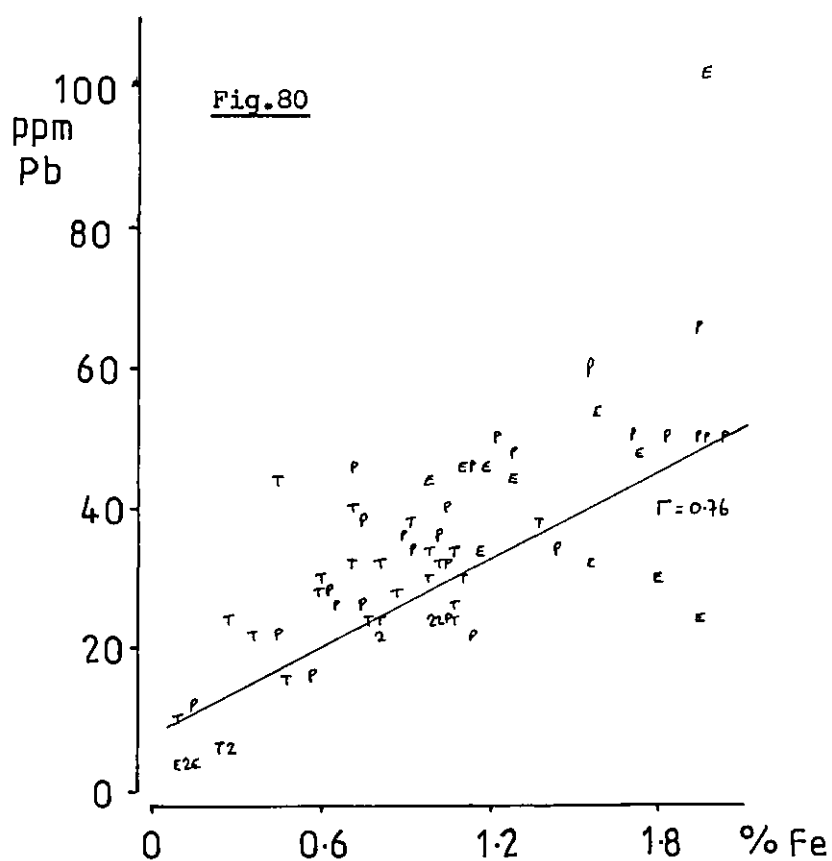
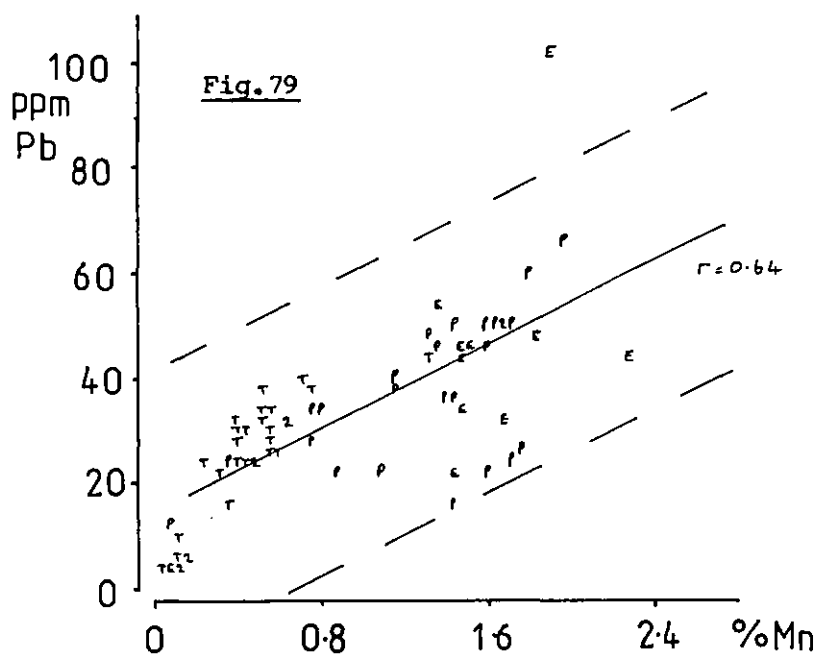


Fig. 76 Zn vs. Mn in the HSF. Symbols as in Figs. 58+63.

Figs 77+78 Al vs. Fe in the HSF of Penrhyn Basin sediments (Fig. 77) and Tokelau sediments (Fig. 78). Symbols as in Figs. 58, 63 and 73.



Figs. 79+80 Pb vs. Mn (Fig. 79) and Fe (Fig. 80) in the HSF of S.W. equatorial Pacific sediments. Symbols as in Figs. 58, 63 and 7. Dashed lines are drawn 3 standard errors from the regression line.

Table 56 Selected element ratios within the HSF. Values
in parentheses represent one standard deviation.
Also presented are significance levels of Student's
t tests to ascertain differences between element
ratios in the Tokelau sediments and combined
Penrhyn and ELI sediments

	Tokelau	Penrhyn	ELI	DOMES B	Significance Level
N	30	21	15	3	
Mn/Fe	0.68(0.46)	1.10(0.35)	1.18(0.41)	1.33(0.37)	0.0001
Cu/Mn	0.024(0.007)	0.016(0.005)	0.021(0.014)	0.046(0.007)	0.006
Ni/Mn	0.016(0.008)	0.019(0.005)	0.021(0.005)	0.038(0.009)	0.02
Co/Mn	0.013(0.003)	0.011(0.003)	0.011(0.001)	0.016(0.003)	0.008
Pb/Mn	0.006(0.001)	0.003(0.0008)	0.003(0.001)		0.0001
Zn/Mn	0.024(0.025)	0.007(0.011)	0.007(0.007)	0.006(0.001)	0.0001
Al/Mn	0.96(0.43)	0.34(0.28)	0.24(0.16)		0.0001
Ti/Mn	0.041(0.095)	0.005(0.003)	0.014(0.022)		0.05
Ti/Fe	0.022(0.046)	0.005(0.003)	0.013(0.017)		< 0.05
Al/Fe	0.55(0.26)	0.34(0.20)	0.27(0.17)		0.002

Al has distinct regional associations. In the Tokelau sediments it is strongly correlated with acid-reducible Fe (Figs. 77 and 78), whilst in the Penrhyn/ELI sediments it shows no relation to either Fe or Mn (not shown).

Ti occurs in low concentrations in the HSF and exhibits no relationship to either Mn or Fe.

Pb is well correlated with both Mn and Fe. The plots of Pb versus Mn (Fig. 79) and Pb versus Fe (Fig. 80) show that for most sediments, Pb is more closely associated with Mn than with Fe, whilst in a smaller number may be associated with Fe. Relative to Mn, Pb is enriched in the Tokelau sediments over the Penrhyn/ELI sediments (Table 56).

By constructing lines parallel to the element:Mn regression line representing 3 standard errors of the estimate it is possible to distinguish HSFs of anomalous composition (Figs. 73-75; 79). These are shown in Table 57. The anomalous sediments fall mainly into two distinct lithological groupings, glass-rich and zeolite-rich, tend to have high Mn/Fe ratios in the HSF and are variously enriched in Cu and/or Ni and depleted in Pb or Co. The disparity of the two dominant sediment types and the non-anomalous compositions of other lithologically similar sediments is rather puzzling and suggests the influence of local environmental conditions. It is worthwhile noting that the enriched elements Mn, Ni and Cu are similarly enriched in diagenetic macronodules, whilst the depleted elements Pb and Co are similarly depleted in macronodules.

11.5.2.3 Comparison with the ammonium oxalate-oxalic acid (AOOA) leach

The AOOA leach developed by Schwertmann (1964) (see Appendix 3) removes amorphous Fe hydroxides and poorly crystalline ferromanganese oxyhydroxides but does not attack crystalline goethite (Landa and Gast 1973), Fe-rich smectite (Heath and Dymond 1977) or CaCO_3 . Whilst some-

Table 57 Sediments with HSFs of anomalous compositions,
defined as falling outside 2 parallel lines
representing plus/minus 3 standard errors of the
estimate above and below the element:Mn regression
line

	Mn/Fe	Pb	Co	Cu	Ni
<u>Glass rich</u>					
V18-275	HIGH ¹		D	E ²	E
V18-276	HIGH	D ²			E
V18-277	HIGH				E
M70-817	HIGH			E	E
<u>Zeolite rich</u>					
AMPH 116	HIGH	D		E	E
AMPH 117	HIGH				
AMPH 126	HIGH	D			
RC13-70			D		
RC13-72					D
<u>Other</u>					
STYX 35				E	
STYX 66			D		
RC13-46	HIGH			D	

¹ High Mn/Fe values are greater than 1.4 (Mean = 1.0)

² D = Depletion)
E = Enrichment) -over Mn

what more specific than the HHA leach of Chester and Hughes (1967), it is nevertheless broadly comparable.

Fourteen sediments were leached with both HHA and AOOA (Table 58). An average of 12.7% ($s = 1.7\%$) of the bulk sediment was AOOA-leachable, compared to 18.9% ($s = 7.5\%$) for HHA, the difference resulting from the removal of CaCO_3 by HHA.

Since approximately 10% more Mn + 5% more Fe are removed by AOOA than HHA (Table 59), it is suggested that AOOA leaches a cryptocrystalline oxide phase additional to those leached by HHA. Elements leached by AOOA in excess of HHA presumably reside in this phase. These include Al, Cu, Ni, Co, Pb, despite poor precision), and, most significantly, Ti, of which 20% is AOOA-leachable compared to less than 1% which is leached by HHA. Comparison of the AOOA and HHA leachates allows the determination of the composition of an AOOA leachable, HHA non-leachable phase (Table 60). The phase is rich in Fe, Al, Ti and Mn and contains trace amounts of Cu, Ni + Co.

The distribution of Ti in the S.W. Pacific sediments corresponds closely to that of volcanic glass (Figs. 62 + 53). The strong correlation between oxalate-leachable Ti and total Ti (Fig. 81) is therefore strongly suggestive of a volcanic source of the leachable Ti. It is envisaged that the phase is a cryptocrystalline Fe-Al-Ti oxyhydroxide resulting from low temperature weathering of volcanic debris, particularly volcanic glass. The greater mobility of Fe and Al during basalt weathering (Colman 1982) suggests that relative to Ti these elements will be preferentially stripped from silicate phases and may form oxyhydroxides (Hart 1973). The higher Al/Mn and Fe/Mn ratios of the HHA fraction of the Tokelau sediments, which are subject to the greatest volcanic influence, indicates that at least some of the volcanically derived Fe and Al enters or forms HHA-leachable phases, whilst the remainder forms an Fe-Al-Ti oxyhydroxide leachable only by AOOA.

Table 58 Comparison of oxalate-soluble and HHA-soluble fractions of S.W. Equatorial Pacific Sediments
Concentrations are in weight %, or ppm of bulk sediment

element sample	% Mn		% Fe		ppm												% Al		% Ti		% leached	
	OX	HHA	OX	HHA	Cu		Ni		Co		Pb		Zn		OX	HHA	OX	HHA	OX	HHA		
K1-2B	0.63	0.53	1.23	0.98	136	112	68	62	70	55	8	34	39	51	0.84	0.58	0.13	0.008	12.6	15.4		
K1-4T	0.52	0.38	1.45	1.00	127	106	63	42	52	51	5	29	47	58	0.90	0.65	0.18	0.004	12.1	19.4		
K1-4B	0.68	0.57	1.42	1.07	119	116	68	62	80	78	8	33	44	98	0.60	0.42	0.22	0.003	12.4	16.2		
K1-5T	0.58	0.52	1.29	0.92	134	128	65	60	61	63	10	38	37	53	0.93	0.67	0.15	0.003	14.0	17.0		
K1-5B	0.66	0.58	1.13	0.87	98	83	80	66	79	72	5	28	41	42	0.62	0.43	0.14	0.003	11.6	18.7		
K1-6B	0.61	0.55	0.92	0.76	138	129	96	92	74	63	3	26	173	390	0.84	0.65	0.10	0.006	11.1	16.8		
C1-15	1.23	1.18	1.44	1.05	198	161	226	195	159	118	5	39	48	50	0.68	0.32	0.096	0.002	15.0	17.8		
KK72-32	1.50	1.46	1.24	1.03	320	277	374	392	199	158	0	36	78	61	0.47	0.28	0.064	0.01	7.5	36.2		
SOTW 5FFA	0.54	0.41	1.39	1.09	135	117	58	51	60	50	5	24	180	181	0.87	0.61	0.17	0.006	11.7	15.0		
AMPH 126	2.54	2.21	2.33	1.79	445	381	500	471	280	237	0	30	82	69	0.39	0.23	0.12	0.007	15.9	29.9		
M70-32	0.84	0.70	1.09	0.73	142	121	154	143	107	90	5	39	284	316	0.37	0.18	0.18	0.003	9.8	6.4		
K2-3	1.52	1.44	1.54	1.24	234	205	301	284	201	178	10	50	57	41	0.55	0.27	0.10	0.00	14.0	18.3		

Table 59 Percentage of element content of bulk sediment
leached by ammonium-oxalate-oxalic acid and by
hydroxylamine hydrochloride - acetic acid.
Data from Table 58.

Element	Oxalate		HHA	
	Mean	S.D.	Mean	S.D.
Mn	97	6	86	9
Fe	22	5	17	4
Cu	54	14	46	12
Ni	65	15	58	18
Co	86	8	77	7
Pb	12	8	73	12
Zn	43	14	47	14
Ca	-	-	51	18
Al	11	3	8	3
Ti	20	7	0.5	

¹ Ca not included in oxalate leach due to poor precision

Table 60 Composition of the oxalate-leachable,
hydroxylamine insoluble phase normalised
to Fe Data from Table 58

<u>Sediment</u>	<u>Composition</u>					
K1-2B	FeMn _{0.48}	Al _{1.04}	Ti _{0.60}	Cu _{0.008}	Ni _{0.002}	Co _{0.005}
K1-4T	FeMn _{0.29}	Al _{0.55}	Ti _{0.42}	Cu _{0.006}	Ni _{0.006}	
K1-4B	FeMn _{0.20}	Al _{0.36}	Ti _{0.62}	Cu _{0.002}	Ni _{0.002}	
K1-5T	FeMn _{0.07}	Al _{0.58}	Ti _{0.35}	Cu _{0.033}	Ni _{0.002}	
K1-5B	FeMn _{0.24}	Al _{0.509}	Ti _{0.43}	Cu _{0.006}	Ni _{0.006}	Co _{0.002}
K1-6B	FeMn _{0.45}	Al _{1.09}	Ti _{0.48}	Cu _{0.010}	Ni _{0.007}	Co _{0.005}
C1-15	FeAl _{1.03}	Ti _{0.26}	Cu _{0.01}	Ni _{0.01}	Co _{0.01}	
KK72-32	FeMn _{0.20}	Al _{1.23}	Ti _{0.32}	Cu _{0.025}	Co _{0.023}	
SOTWX 5FFA	FeMn _{0.30}	Al _{1.01}	Ti _{0.65}	Cu _{0.008}	Ni _{0.004}	Co _{0.004}
AMPH 126	FeMn _{0.62}	Al _{0.30}	Ti _{0.22}	Cu _{0.013}	Ni _{0.005}	Co _{0.008}
M70-32	FeMn _{0.25}	Al _{0.53}	Ti _{0.47}	Cu _{0.06}	Ni _{0.002}	Co _{0.009}
K2-3	FeMn _{0.19}	Al _{1.30}	Ti _{0.41}	Cu _{0.01}	Ni _{0.006}	Co _{0.01}

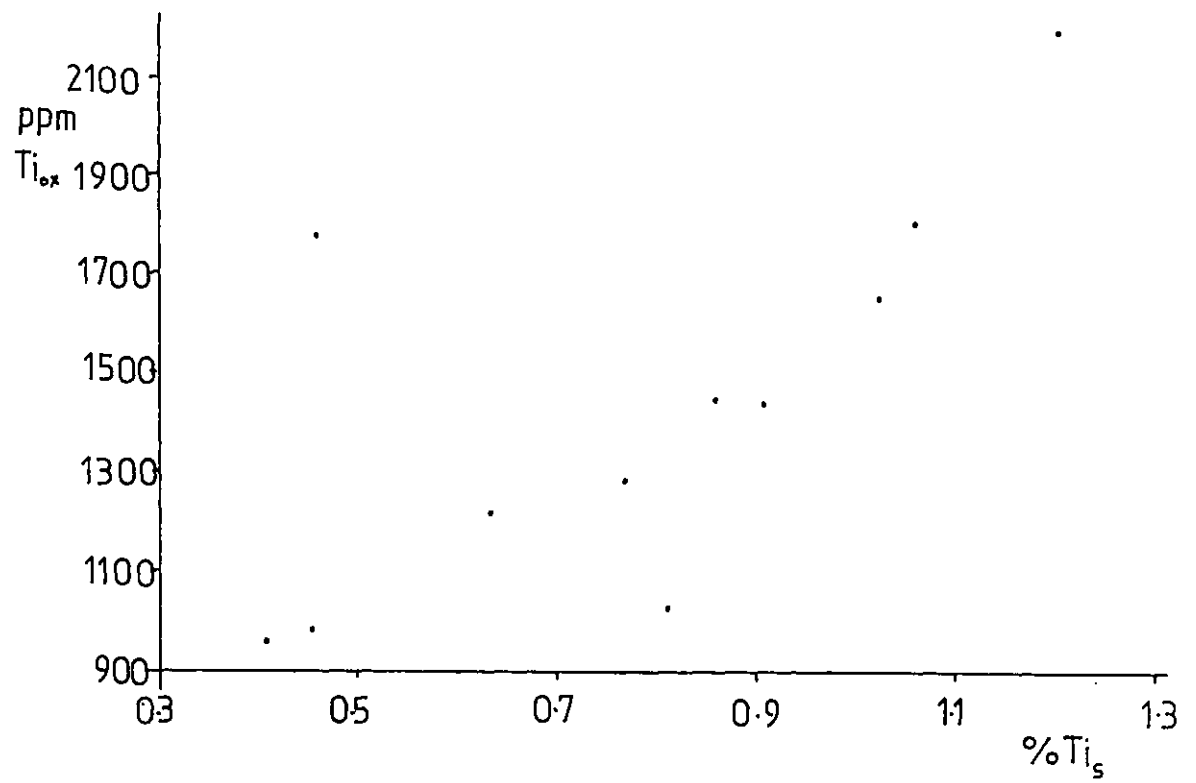


Fig.81 Plot of Ti soluble in ammonium oxalate-oxalic acid (Ti_{ox}) versus total Ti in bulk sediment (Ti_s).

11.5.2.4 Element ratios in the HSF

Due to variations in the proportion of hydrogenous material within the present suite of sediments, it is more instructive to examine element ratios in the HSF than absolute element abundances. These ratios (Table 56), which reflect processes of supply and diagenesis, exhibit significant regional variation. Whilst the Penrhyn and ELI sediments are very similar in composition, Tokelau Cu/Mn, Co/Mn, Pb/Mn, Al/Mn and Al/Fe ratios are greater than their Penrhyn-ELI counterparts (99% confidence level), and vice versa for the Mn/Fe and Ni/Mn ratios. The Ti/Mn and Ti/Fe ratios show little regional variability, but are variable within regions. The regional consistency of the Ti/Mn and Ti/Fe ratios is surprising in view of the non-uniform volcanic influence throughout the region. Whilst there appears to be an important volcanic supply of Ti into oxide phases (Section 11.5.2.3), it seems that the phase is non-leachable by HHA, but is leachable by AOOA. Regional variations in Ti/Mn, related to volcanism, can therefore be observed only with the AOOA leach. The Zn/Mn ratios of the Penrhyn and ELI sediments are identical, but much lower than the ratio in the Tokelau sediments. However, the large standard deviation in the Tokelau sediments is suggestive of Zn contamination.

Important differences exist between the SW Pacific sediments and the DOMES sediments (Table 56). The Ni/Mn and Cu/Mn ratios are greater in the DOMES sediments, whilst the Co/Mn ratio is clearly comparable to the values throughout the SW Pacific. The DOMES Mn/Fe and Zn/Mn ratios are similar to those in the Penrhyn-ELI sediments, but the Mn/Fe ratio is very different to the same ratio in the Tokelau sediments.

11.5.2.5 Mn/Fe ratio

The mean Mn/Fe ratio of the HSF $(\text{Mn/Fe})_H$ of Tokelau sediments (0.68) is significantly less than those of the Penrhyn sediments (1.10), ELI sediments (1.18) or DOMES

sediments (1.3) (Table 56, Fig. 82).

Away from hydrothermally active areas, four processes may operate to affect the $(\text{Mn}/\text{Fe})_{\text{H}}$ ratio in surface sediments:-

1. Diagenetic remobilisation of Mn under reducing conditions with subsequent reprecipitation in a surficial oxic layer (Lynn + Bonatti 1965, Li et al. 1969, Calvert and Price 1972).
2. A regionally variable supply of Mn and Fe from the water column.
3. Oxic diagenetic reactions between biogenic silica and Fe-Mn oxyhydroxides (Heath and Dymond 1977, Lyle et al. 1977).
4. Low temperature weathering of volcanic material (halmyrolysis) (Goldberg + Arrhenius 1958, Bonatti 1963, Hart 1970, 1973).

To examine each in turn:-

11.5.2.6 Remobilisation of Mn

The role of diagenesis in redistributing Mn in the sediment column is well established (Lynn and Bonatti 1965, Li et al. 1969, Calvert and Price 1972). Under regions of high productivity, the reduction of Mn oxides in poorly oxic sub-surface sediments causes an upwards migration of Mn^{2+} along concentration gradients with subsequent reprecipitation in a thin surficial oxic layer. Fe is not similarly remobilised since it is reduced at Eh values sufficiently low that it is fixed as FeS .

Bender (1971) and Elderfield (1976) have calculated that upwards diffusion cannot contribute significantly to the observed accumulation rates of Mn in surface sediment in regions where the oxic layer is greater than approximately 20 cm thick. The thickness of the oxic layer is a function of the supply of organic matter and the rate of sedimentation (e.g. Müller and Suess 1979). Both are extremely low in the SW Pacific, and the oxic layer would be expected to greatly exceed 20 cm. This is supported by observational evidence that four 50 cm

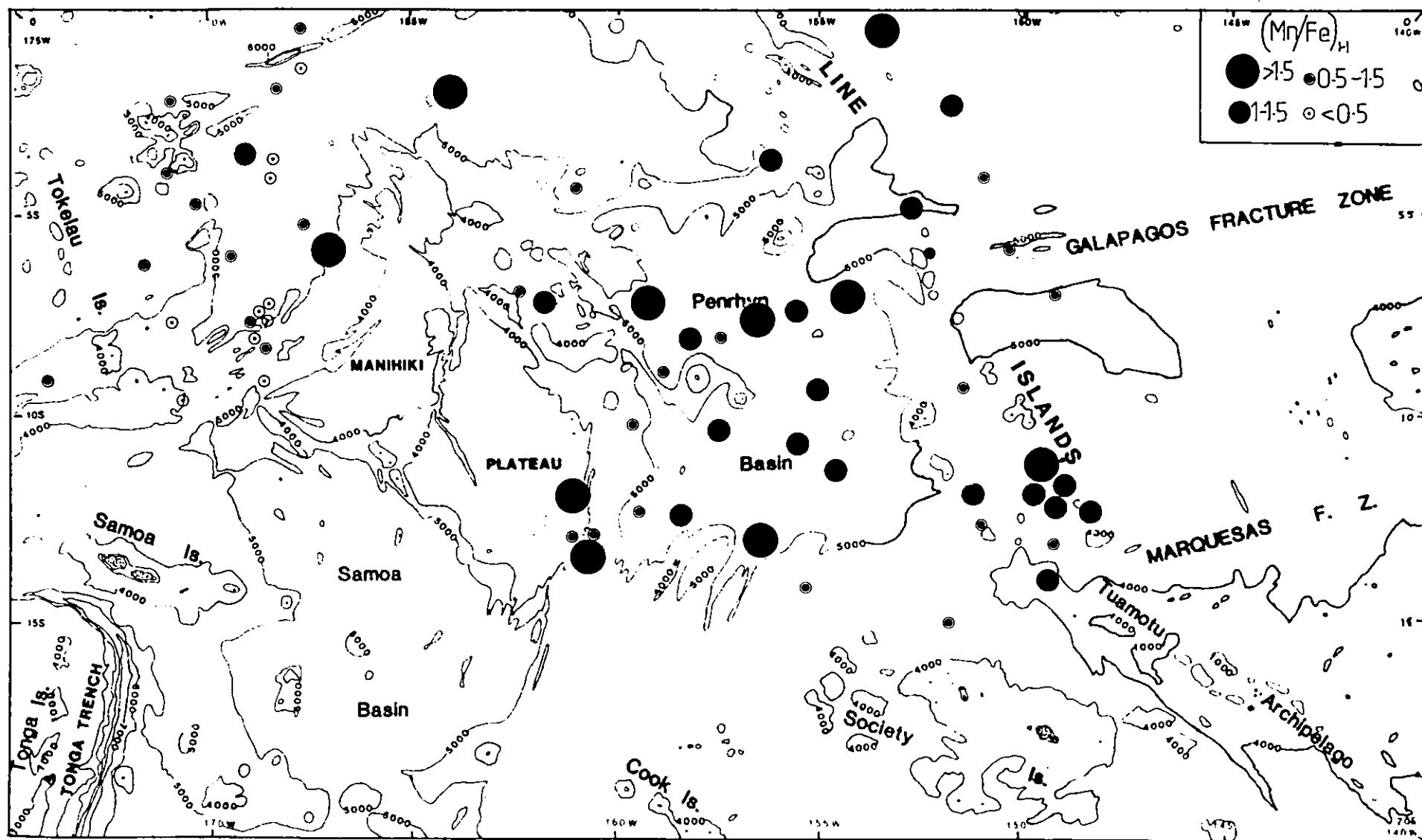


Fig.82 Distribution of the Mn/Fe ratio of the HSF in surface sediments of the S.W. equatorial Pacific.

cores from the equatorial Tokelau region (K1-2, K1-4, K1-5, K1-6) did not exhibit the discolouration which is associated with Mn or Fe reduction.

11.5.2.7 Supply from the water column

Calculations of metal fluxes to the sediment-water interface (Chapter 9) suggest that a large proportion of Mn and Fe is supplied in association with faecal material. On the basis of the only analyses available (Fowler 1977, Spencer et al. 1978), the non-aluminosilicate fraction of this material may have a Mn/Fe ratio of 0.2-0.3. A second source of Mn and Fe is from colloidal ferromanganese oxides accumulating directly from the water column, which may be assumed to have a similar composition to the LI crusts (Mn/Fe = 1.1 Chapter 3), which are also accumulating directly from the water column.

Regional variations in the relative rates of supply of the two fractions will cause a variation in the Mn/Fe ratio of the HSF. The faecal flux may be expected to be relatively more important in zones of high productivity; however, productivity is no greater in the Tokelau region than in the Penrhyn Basin, where $(\text{Mn/Fe})_H$ values are greater. Further, the importance of other processes is suggested by the high Mn/Fe ratio in the HSF of DOMES area sediments, which underlie higher productivity waters than the SW Pacific sediments.

11.5.2.8 Oxic diagenesis

Working on Bauer Basin sediments, Heath and Dymond (1977) have proposed a reaction in which hydrothermal Fe oxyhydroxides react with biogenic silica in surficial sediments to form an Fe-rich smectite. Thermodynamic considerations (Bischoff and Rosenbauer 1977) suggest that the proposed reaction is feasible under deep ocean

conditions of pH and Eh, which indicates that the reaction may occur over large areas where the reactants are in sufficient supply. For example, Hein et al. (1979) have proposed that the Fe-rich montmorillonite found in the DOMES sediments has formed in this manner.

In the S.W. Pacific smectite is the most abundant clay mineral. As outlined in Chapter 10, its abundance relative to other, dominantly detrital, clay minerals increases from west to east, and in the east of the region, from south to north. The chemical composition of the smectite and its antipathetic relation to regional volcanism suggests that the combination of biogenic silica and Fe oxyhydroxide is an important formation mechanism, even in regions of low productivity. Whilst it occurs throughout the region, the relative importance of the reaction is greatest in more slowly accumulating sediments (cf. Calvert et al. 1978).

Because Mn is not readily accepted by the smectite structure, Mn associated with Fe oxyhydroxides participating in diagenesis remain in the sedimentary oxide phases (Eklund 1974), effectively increasing the $(\text{Mn/Fe})_H$ ratio. Under conditions of constant relative supply of Mn and Fe, enhanced diagenesis will yield an increased $(\text{Mn/Fe})_H$ ratio. This is strongly suggested to be the case in the SW Pacific by the high positive correlation between % smectite ($\equiv$ diagenesis) and $(\text{Mn/Fe})_H$ (Fig. 83).

Two factors may confuse this simple relationship:- first, a regionally variable supply of Mn and Fe oxyhydroxides, and second, a variable supply of biogenic silica. The first point is considered in Section 11.5.2.7. Concerning the latter, Cole (1982) has suggested that in the Bauer Basin the limiting factor in authigenic smectite formation is the supply of biogenic silica. An enhanced supply of silica may therefore increase the amount of smectite formed in unit time and heighten its relative importance in the clay fraction.

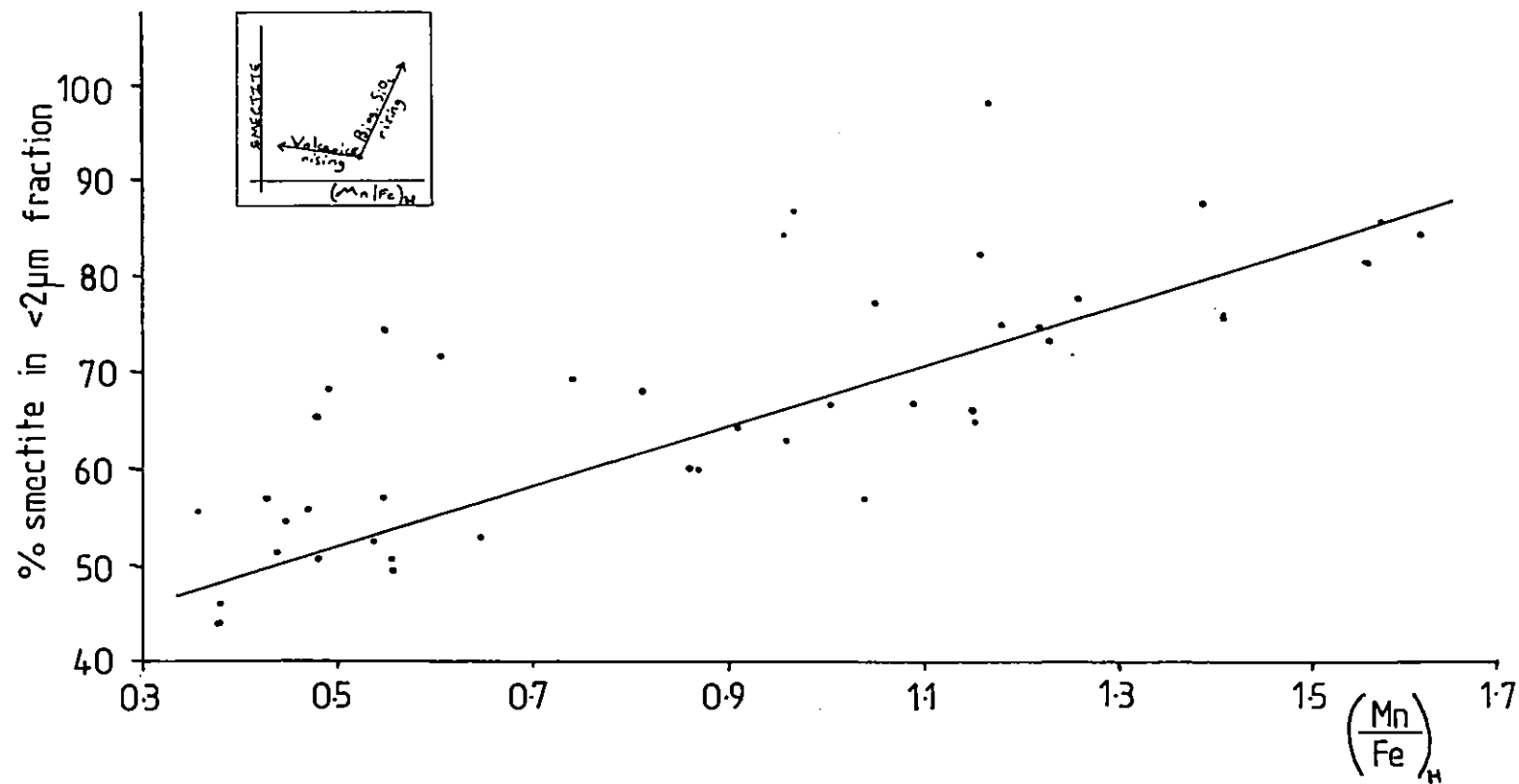
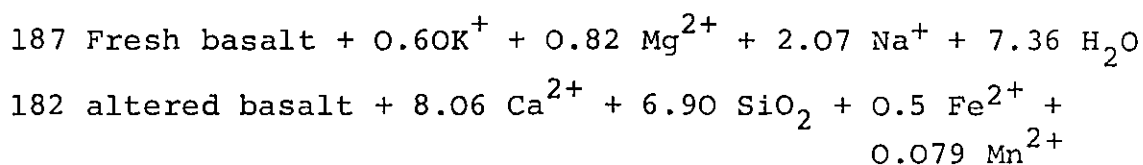


Fig.83 Plot of the Mn/Fe ratio in the HSF versus the smectite content of the < 2μm fraction of S.W. equatorial Pacific surface sediments. The inset shows the probable directional effects of increasing abundances of volcanic glass and biogenic silica in the sediments. The regression line is drawn by eye.

11.5.2.9 Volcanic Supply

It is well established that both Fe and Mn are leached from basalt under conditions of hydrothermal circulation (e.g. Bostrom et al. 1969, Corliss 1971, Edmond et al. 1979). The process of low temperature weathering, or halmyrolysis, is however less well documented. Hart (1970, 1973) has addressed the problem and has proposed the following reaction, expressed in units of 10^{14} gy^{-1} :-



According to this reaction, 60 times more Fe than Mn is released by halmyrolytic processes. At seawater Eh and pH, the Fe will be in the trivalent state, and will presumably form oxyhydroxides in the sediment.

There is a good qualitative inverse relationship between the distribution of volcanic glass in sediments and observed $(\text{Mn/Fe})_H$ ratios (Figs. 53+82). Further, whilst the Tokelau sediments, which have a greater volcanogenic component than the Penrhyn-ELI sediments, are depleted in both Mn and Fe relative to them, they exhibit a greater depletion in Mn than Fe. Although this is reasonable circumstantial evidence for a halmyrolytic source of Fe, it is difficult on the basis of Mn/Fe ratios to differentiate between volcanogenic + oxic diagenetic influences. For example, the lower $(\text{Mn/Fe})_H$ ratios in the Tokelau sediments could be interpreted in terms of either an increased volcanogenic influence or decreased diagenesis. The effects of each are cumulative, since volcanogenic sediments accumulate more rapidly and will be less subject to diagenesis.

One way of examining volcanogenic inputs is to look at Ti, which has a strong association with volcanic debris (Goldberg + Arrhenius 1958, see Section 11.3). Although little Ti is leached by HHA, the AOOA leaches significant quantities of Ti (Section 11.5.2.3). The plot of

oxalate - leachable Ti versus total Ti (Fig. 81) shows a very strong positive correlation, suggesting that there is a strong volcanic input of Ti to the sedimentary oxides. Since Fe is more mobile than Ti in the weathering process (Hart 1973, Colman, 1982), a volcanogenic source of Fe may be inferred. Some of the Fe enters HHA-leachable phases, yielding lower Mn/Fe ratios in the HSF.

The effect of the volcanic supply of Fe on the smectite: $(\text{Mn/Fe})_H$ plot (Fig. 83, inset) is to enhance the positive correlation, since the effect is greatest in the smectite-poor Tokelau sediments. It is interesting to note that almost all the sediments lying above the general trend contain either large quantities of volcanic glass or biogenic silica, the presence of which may increase the smectite/ $(\text{Mn/Fe})_H$ ratio.

To summarize, two simultaneous processes operate to affect the Mn/Fe ratio of the HSF - a diagenetic reaction between Fe oxyhydroxide and biogenic silica, which increases the Mn/Fe ratio, and a halmyrolytic supply of Fe superimposed upon the water column supply, which reduces the Mn/Fe ratio. The observed ratio therefore reflects the balance of these processes; whilst diagenesis occurs throughout it is most important in the slowly accumulating sediments in the Penrhyn - ELI region. Halmyrolysis is important only in the Tokelau sediments.

11.5.2.10 Element/Mn ratios

Element/Mn ratios and their regional variations reflect relative rates of elemental supply and the effects of repartitioning during early diagenesis. Previous discussions (Sections 10.3.4 + 11.5.2.8) suggest that one important diagenetic process is the combination of Fe oxyhydroxide with biogenic silica to form an Fe-rich montmorillonite. Analyses of smectites from SW Pacific sediments (Tables 42 and 43) yield approximate ratios of $\text{Al/Mn} = 33$, $\text{Pb/Mn} = 0.05$, $\text{Zn/Mn} = 0.13$, $\text{Cu/Mn} = 0.20$, $\text{Ni/Mn} = 0.04$ and $\text{Co/Mn} = 0.01$. The smectite Al/Mn, Pb/Mn, Zn/Mn and Cu/Mn ratios are greater than their counterparts

in the HSF, and are approximately the same for Ni/Mn and Co/Mn.

A proportion of the trace metals will occur in the smectite's ion-exchangeable positions, whilst the rest will occur in lattice positions (Hein et al. 1979b). Assuming that the lattice trace metals are derived from the oxyhydroxides, enhanced diagenesis superimposed on a constant relative rate of metal supply will decrease the Cu/Mn, Pb/Mn and Zn/Mn ratios in the HSF, but will not affect the Ni/Mn and Co/Mn ratios. The observed element/Mn ratios in the SW Pacific (Table 56) are consistent with a greater diagenetic influence within the Penrhyn-ELI sediments over the Tokelau sediments.

The Cu/Mn and Ni/Mn ratios of the DOMES area HSF are greater than those of the SW Pacific sediments (Table 56), despite the likely importance of diagenetic reactions in that region (Hein et al. 1979). It is therefore necessary to invoke an increased supply of Cu and Ni relative to Mn in the DOMES region.

Chapter 12 Nodule geochemistry and mineralogy

12.1 Introduction

Work over the past 15 years has clearly demonstrated that nodules may receive metals both directly from the water column and from within associated sediments (Price + Calvert 1970, Raab 1972, Calvert + Price 1977, Halbach et al. 1981a). Early diagenetic reactions within the sediment column release and remobilise metals which can contribute significantly to the growth of nodule surfaces in contact with sediment (Calvert and Price 1977). Mineralogical and chemical determinations (Calvert and Price 1977, Usui 1979, Halbach + Özkara.1979, Moore et al. 1981) indicate that the resulting diagenetic precipitate is predominantly composed of the phyllomanganate todorokite, which is rich in Mn, Cu, Ni + Zn, whilst the material precipitating directly from the water column consists of an intimate mixture of the disordered Mn oxide 5MnO_2 and amorphous $\text{FeOOH}\cdot\text{H}_2\text{O}$ in roughly equal proportions.

Variations in the relative importance of the two growth processes yield nodules which may be classified according to their genesis into (from Halbach et al. 1981a):-

1. early diagenetic type - metals supplied dominantly from underlying sediments.
2. hydrogenetic type - metals supplied dominantly from the water column.
3. mixed type - metals supplied both from the underlying sediments and from the water column.

Early diagenetic and mixed type nodules, which are of most interest economically, occur mainly in areas bordering regions of high surface water productivity. They are found most extensively in the NE equatorial Pacific (NEP), but also occur in the SE and central south Pacific (Halbach et al. 1980, Pautot and Melguen 1979).

The SW equatorial Pacific (SWP) is positioned on the edge of the equatorial high productivity zone, but has received less attention than the other Pacific equatorial regions. The area therefore yields an opportunity to test the validity of the hypotheses put forward to relate nodule chemistry to the sedimentary environment. In particular, the analysis of a suite of Fe-Mn encrustations from the adjacent Line Islands Archipelago enables a good estimate to be made of the composition of the 'hydrogenetic' component of the nodules. From this it may be possible to ascertain more precisely the role of associated sediments in determining nodule composition.

12.2 The data set and methods of analysis

Thirty nine nodules collected by free-fall grab from 25 sites on the 1980 CCOP/SOPAC cruises plus 22 nodules obtained from existing collections at Scripps Institution of Oceanography and Lamont Doherty Geological Observatory were analysed chemically and mineralogically. Samples were finely ground and dried at room temperature over silica gel. Analysis for Mn, Fe, Cu, Ni, Co, Pb, Zn, Ca, Al and Ti was by atomic absorption spectrophotometry. Accuracy, as determined by comparison with German nodule standards, was generally better than 10%, whilst precision was better than 3% for each element (Appendix 3). Mineralogical analyses were made by subjecting unoriented mounts to Fe K α radiation and run at $1^{\circ}2\theta \text{ min}^{-1}$ from $5-90^{\circ} 2\theta$.

A further 147 analysis from the Scripps Data Bank (provided by J.Z. Frazer) were used in plotting element distribution maps and in determining correlation coefficients between individual elements.

Finally, 9 samples were leached with acidified hydroxylamine hydrochloride (HHA) and the leachates analysed by atomic absorption spectrophotometry for the standard ten element suite (Appendix 3).

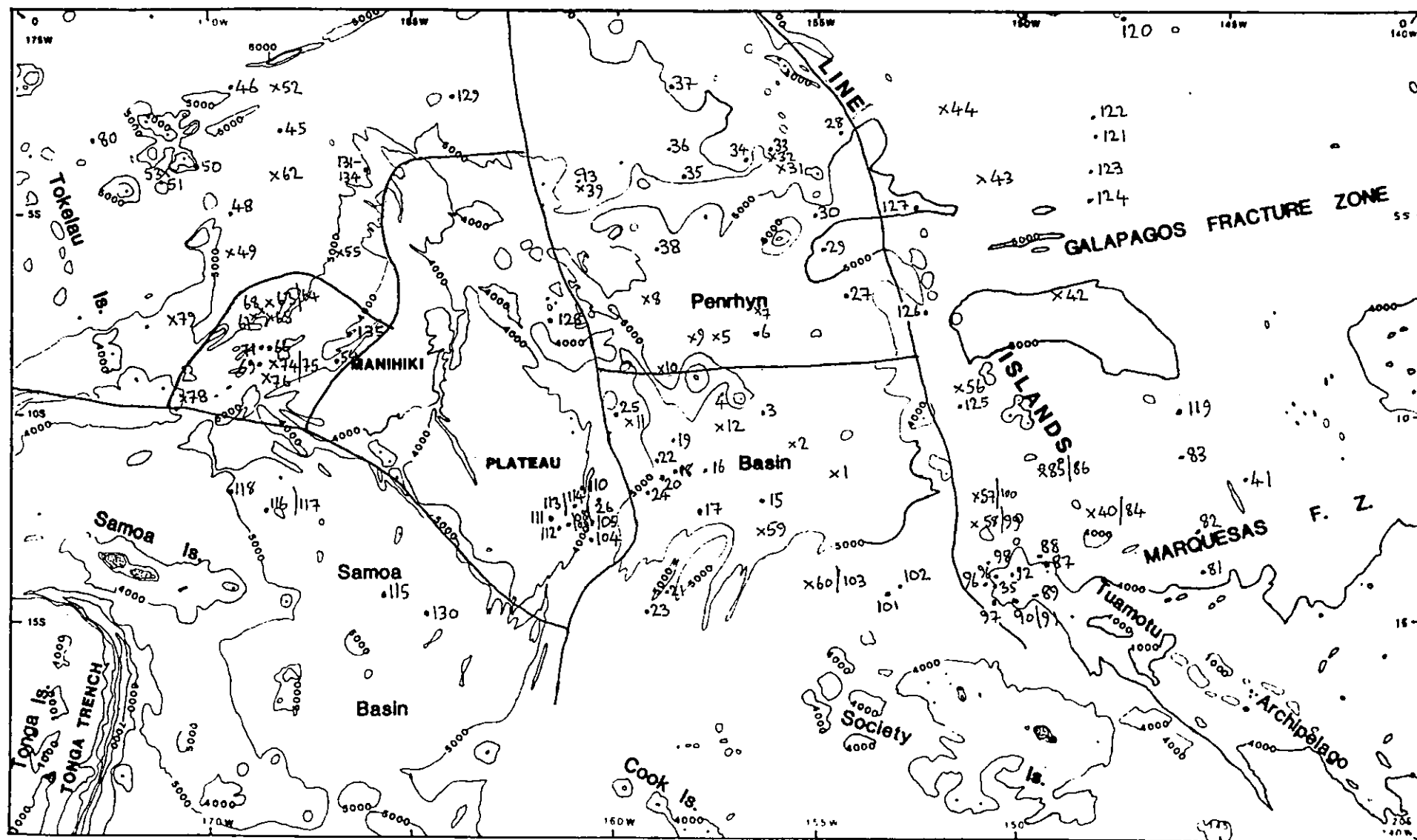


Fig.84 Nodule sample locations, showing regional divisions of the area (see Fig.48). Sites at which associated sediments were obtained are marked with an 'x'. Numbers refer to stations listed in Appendix 4.

12.3 Areal compositional variations

Whilst the composition of nodules varies both within individual nodules (e.g. Raab 1972, Sorem and Foster 1973) and over small distances (e.g. Cronan and Tooms 1967, Calvert et al. 1978), analysis of larger scale variability is worthwhile since it may elucidate patterns of processes and element supply which may be related to larger scale oceanographical features.

Both Glasby (1981) and Exon (in press) have stressed the latitudinal variability of nodule composition in the SWP. Both noted an increase in nodule grade (i.e. Ni + Cu content) towards the equator, with grades above 2% confined mainly to a zone between 5°S and 6°N in the eastern Central Pacific Basin. In order to examine longitudinal in addition to latitudinal compositional variability, the region was subdivided into the area to the east of the LIA (ELI), the North and South Penrhyn Basins, the Tokelau region, the Samoan Passage and the Samoan Basin (Fig. 84).

Mean compositions of nodules from each area are shown in Table 61. Nodules from the N. Penrhyn Basin and ELI area are compositionally similar, but distinct from S. Penrhyn Basin and Tokelau nodules, which are also closely comparable. On average, ELI and North Penrhyn nodules have a similar Mn/Fe ratio to NEP nodules, but are depleted in Cu and Ni. They are still enriched in Cu and Ni compared to the S. Penrhyn and Tokelau nodules, but have lower Co, Pb and Ti contents.

Samoan Passage nodules have compositions closer to those of the South Penrhyn Basin than the North Penrhyn Basin, but are slightly depleted in Ni and enriched in Fe and Ti. This trend is continued into the Samoan Basin, where nodules exhibit the lowest Cu, Ni and Co contents of anywhere in the region and have Mn/Fe ratios lower than 1.

The Mn/Fe ratio of nodules is an interesting parameter since away from centres of hydrothermal activity

Table 61 Mean compositions of nodules from the S.W. Pacific and the N.E. Equatorial Pacific, plus the mean composition of Fe-Mn crusts dredged from deeper than 2000 m on the Line Islands Archipelago

	← ppm →							
	%Mn	%Fe	Cu	Ni	Co	Pb	Zn	%Ti
E. Line Islands	23.0	10.4	0.69	0.90	0.25	460	1080	0.47
N. Penrhyn Basin	21.0	10.3	0.69	0.80	0.21	460	1010	0.77
S. Penrhyn Basin	17.4	14.8	0.26	0.46	0.36	890	520	1.02
Tokelau Region	18.4	15.2	0.37	0.48	0.32	720	640	1.27
Samoan Passage	17.5	17.6	0.23	0.33	0.36	950	620	1.53
Samoan Basin ¹	17.3	19.6	0.17	0.23	0.23	-	-	-
N.E. Pacific ¹	22.4	8.1	1.16	1.02	0.25	-	-	-
LI Crusts	20.4	17.0	0.15	0.39	0.55	1020	590	1.20

¹Data from Glasby et al. (1981)

it represents a useful index of diagenetic influence (Price and Calvert 1970). The distribution of Mn/Fe ratios in SWP nodules (Fig. 85) shows that high values (>3.0) occur only within 3° of the equator at 175°W but are increasingly widespread towards the east, occurring between 0 and 12°S at 145°W . Interspersed with the higher values are ratios between 1 and 2, serving to stress the importance of local variations that are superimposed upon the more general trends.

Many Mn/Fe values cluster around 1 - 1.3, similar to that of the LI crusts (Mean = 1.2). Values lower than the mean for the crusts are found in the SW Penrhyn Basin, the Samoan Basin and Passage and the Tokelau region with a minimum observed value of 0.57 (Sample Cl-5).

12.4 Mineralogy

The predominant Mn oxide minerals observed in Fe-Mn nodules are todorokite, a $10\text{\AA}$ manganate characterised by diffraction lines at $9.8\text{\AA}$, $4.9\text{\AA}$, $2.4\text{\AA}$ and $1.4\text{\AA}$, poorly crystalline δMnO_2 , denoted by weak and broad lines at 2.44 and $1.42\text{\AA}$ and the less frequently observed birnessite, a $7\text{\AA}$ manganate characterised by lines at 7.2 and $3.6\text{\AA}$ (Büser and Grutter 1956, Giovanoli and Bürki 1975, Burns and Burns 1977, 1979).

In addition to their occurrence in diagenetic nodules (Halbach et al. 1981a), well crystalline todorokite and birnessite have both been identified in hydrothermal Mn crusts (Corliss et al. 1978, Lonsdale et al. 1980, Cronan et al. 1982) and in micronodules (Dymond and Eklund 1978, Glover 1977). On the other hand, δMnO_2 has not been found in hydrothermal deposits, but is the dominant Mn oxide in hydrogenous crusts (Craig et al. 1982, this work) + hydrogenetic nodules (Halbach et al. 1981a).

Crystalline Fe oxides are rarely found in marine Fe-Mn deposits; the most common Fe oxide is amorphous Fe oxyhydroxide, $\text{FeOOH} \cdot x \text{H}_2\text{O}$.

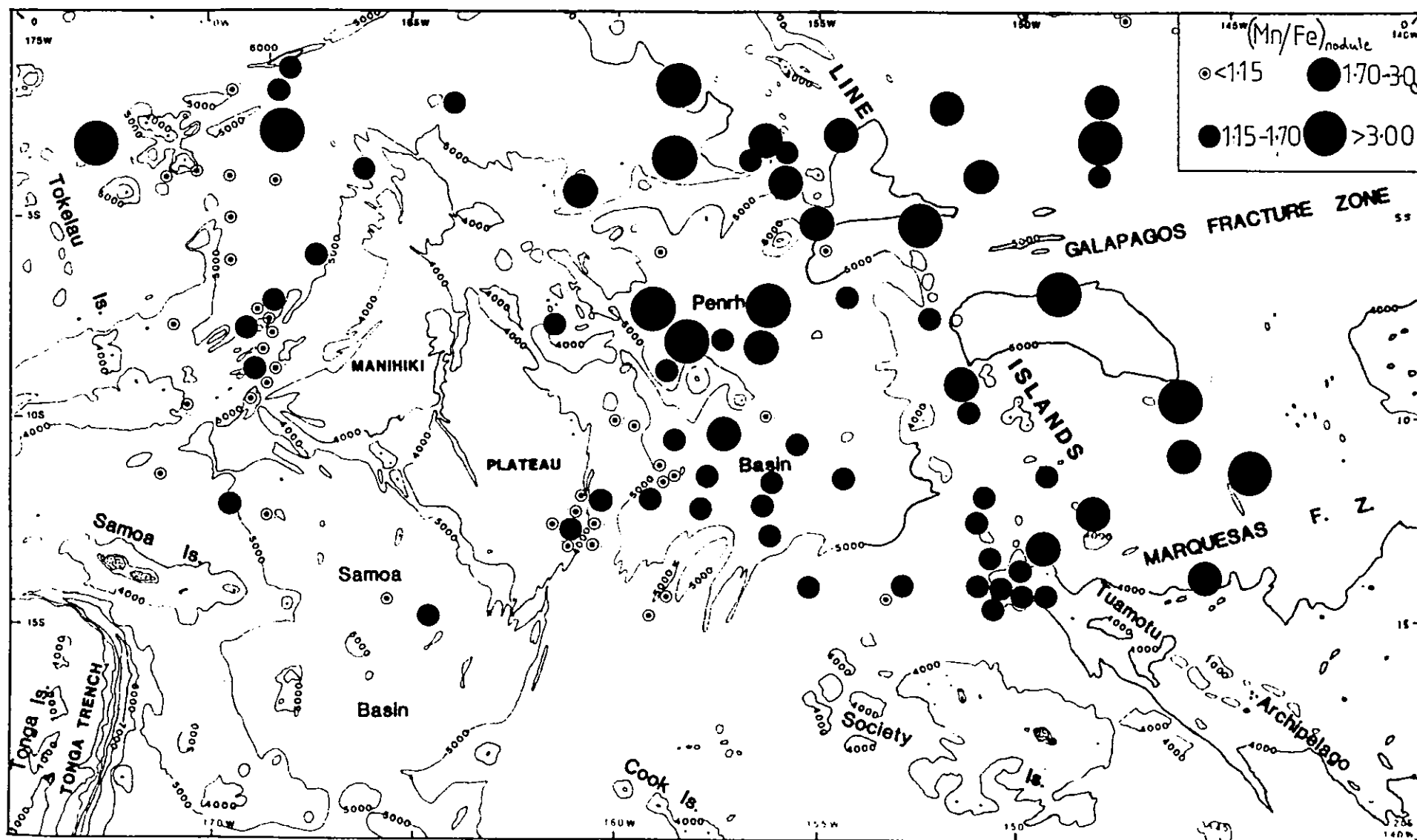


Fig.85 Distribution of Mn/Fe ratios in ferromanganese nodules of the S.W. equatorial Pacific.

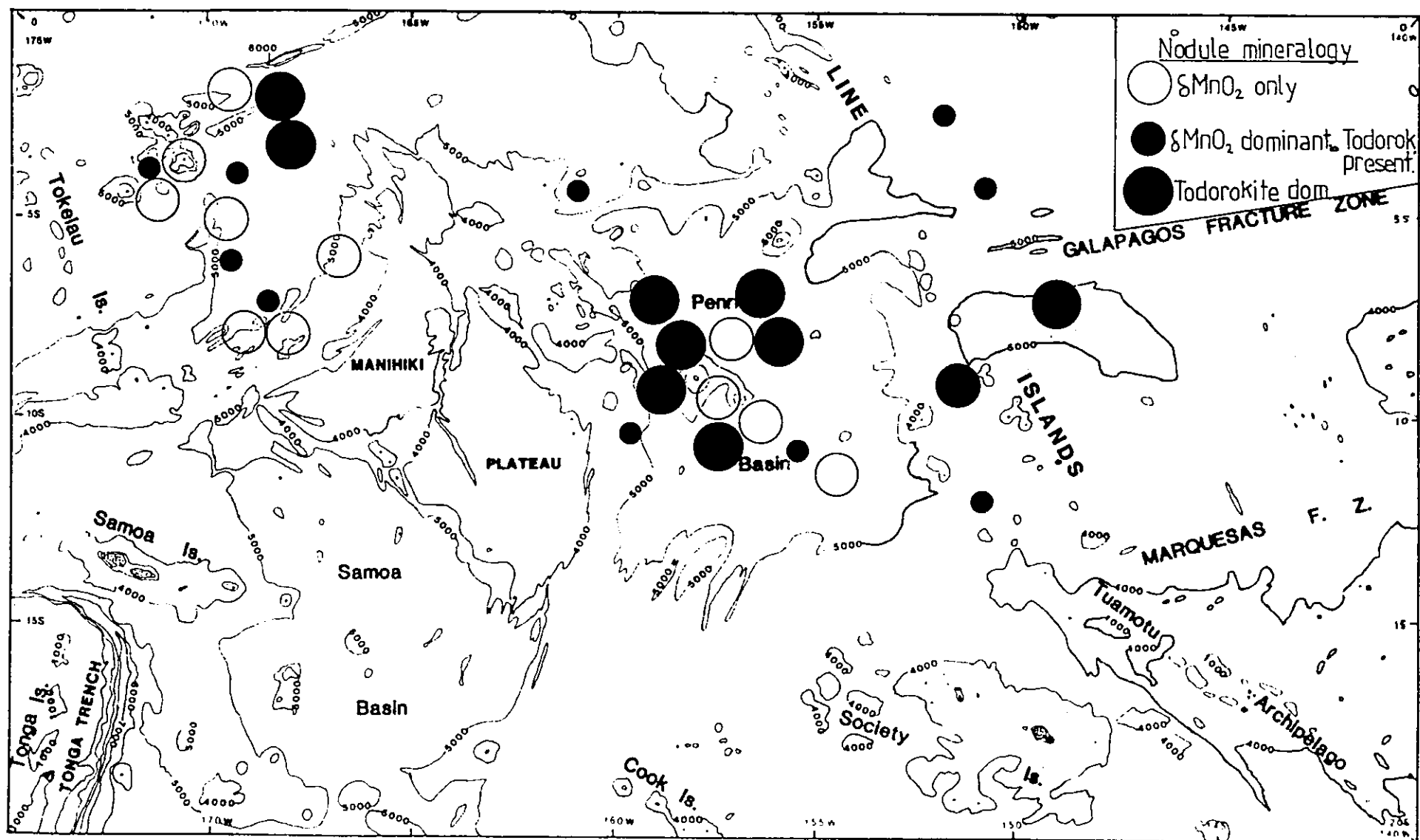


Fig.86 Distribution of todorokite and δMnO_2 in ferromanganese nodules from the S.W. equatorial Pacific.

Recent work using high resolution transmission electron microscopy has shown that marine todorokite is structurally identical to continental todorokites (Turner and Buseck 1981, Turner et al. 1982), confirming earlier predictions (Burns and Burns 1977, 1979) that todorokite has a tunnel structure comprising mainly triple chains of edge -shared MnO_6 octahedra. Crystal chemical considerations indicate that the tunnels can accommodate large cations (Ba^{2+} , K^+ , Na^+ , Ca^{2+}) and water molecules. Further, calculations of Mn:O ratios in todorokites (e.g. Straczek et al. 1960) and comparisons with synthetic phases (Giovanoli et al. 1975) indicate that divalent cations of a similar dimension to Mn^{2+} are essential to the todorokite structure. In continental and hydrothermal todorokites these positions are filled mainly with Mn^{2+} . In other marine todorokites, Cu^{2+} , Ni^{2+} , Zn^{2+} and Mg^{2+} may substitute for Mn^{2+} .

In the present suite of samples, todorokite was identified in 25 of 47 nodules, with the other 22 showing δMnO_2 as the sole Mn oxide mineral. Weak and broad $7\text{\AA}$ reflections were noted in samples C1-13, K3-1 and STYX 56, and probably indicate small quantities of birnessite.

Since todorokite and δMnO_2 share 2.4 and $1.4\text{\AA}$ reflections, it is difficult from X-ray diffraction alone to ascertain the latter in the presence of the former. It is however possible to obtain a crude measure of their relative importance by measuring the $9.8\text{\AA}/1.4\text{\AA}$ peak height ratios on X-ray diffractograms (Lyle et al. 1977). In this way an outline of each mineral's areal distribution may be obtained (Fig. 86). Fig. 86 shows that todorokite has an analogous distribution to that of high Mn/Fe ratios (Fig. 85). It is important between 0 and 3°S in the Tokelau region, but occurs between 0 and 10°S in the Penrhyn Basin and ELI region. Nodules with δMnO_2 only occur throughout the region. No relationship was observed between mineralogy and depth (Cronan and Tooms 1969).

12.5 Interelement relationships

Using all the available data for SWP nodules the element correlation matrix shown in Table 62 was constructed. The well known positive linear correlations between Mn, Cu, Ni and Zn, and between Fe, Co, Pb and Ti were observed.

Since there is a relationship between Mn oxide mineralogy and nodule composition, it is more instructive to examine element associations in mineralogical groups (Tables 63 and 64). Significant correlations are observed between the following element groups:-

SMnO₂:- Mn - Co - Ni - Ca
Fe - Ti - Pb
(Mn and Fe unrelated)

Todorokite:- Mn - Cu - Ni - Zn
Fe - Ti - Co - Pb
(Mn and Fe negatively correlated)

Scatter plots show these relationships visually (Figs. 87 - 90).

At a given Mn content, todorokite-rich nodules contain a greater concentration of Cu, Ni and Zn than SMnO₂-rich nodules. The ratio of Cu:Mn and Ni:Mn is, however, rather constant in the todorokite-rich nodules at all Mn contents, although the Zn:Mn ratios are more variable (Figs. 91-93).

The Co content of todorokite-rich nodules is low and far more constant than of SMnO₂-rich nodules (Fig. 90). As the Mn content of todorokite-rich nodules increases, the Co/Mn ratio decreases, whilst the Co/Mn ratios of SMnO₂ ratio is independent of the Mn content (Fig. 94). Ti and Pb plot in a similar way to Co.

Certain interelement relationships are of particular interest:-

1. Ti and Pb are associated with Fe in both todorokite-rich and SMnO₂-rich nodules. In contrast, Ti exhibits no specific association with either Mn or Fe in the SMnO₂-rich LI crusts, whilst Pb shows a closer association with Mn than with Fe.

Table 62 Element correlation matrix for Fe-Mn nodules using all available data. Underlined values are significant at 0.001 level

	Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb
Fe	<u>-0.45</u>								
Ca	0.19	0.23							
Al	-0.31	<u>-0.51</u>	-0.17						
Ti	<u>-0.50</u>	<u>0.91</u>	0.27	-0.40					
Cu	<u>0.78</u>	<u>-0.74</u>	0.02	0.13	<u>-0.75</u>				
Ni	<u>0.75</u>	<u>-0.78</u>	-0.05	0.15	<u>-0.73</u>	<u>0.91</u>			
Co	-0.16	<u>0.52</u>	<u>0.38</u>	<u>-0.53</u>	<u>0.65</u>	<u>-0.53</u>	<u>-0.47</u>		
Pb	-0.37	0.79	0.26	<u>-0.44</u>	<u>0.80</u>	<u>-0.70</u>	<u>-0.69</u>	<u>0.72</u>	
Zn	<u>0.81</u>	<u>-0.65</u>	0.01	-0.06	<u>-0.56</u>	<u>0.88</u>	<u>0.83</u>	<u>-0.51</u>	<u>-0.61</u>

r(99.9% significance)

Mn, Fe, Cu, Ni, Co	N = 200	0.24
Pb, Zn	- 140	0.28
Ca	- 100	0.33
Al	- 85	0.35
Ti	- 60	0.41

Table 63 Element correlation matrix for Fe-Mn nodules containing 5MnO_2 as the sole Mn oxide mineral. No. of samples = 25 Underlined values are significant at the 0.001 level

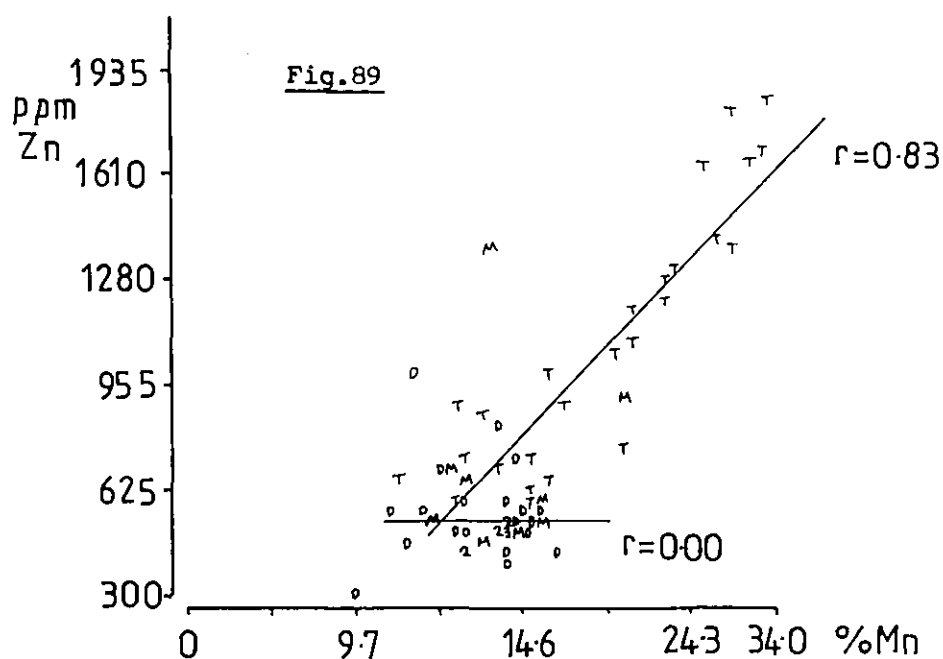
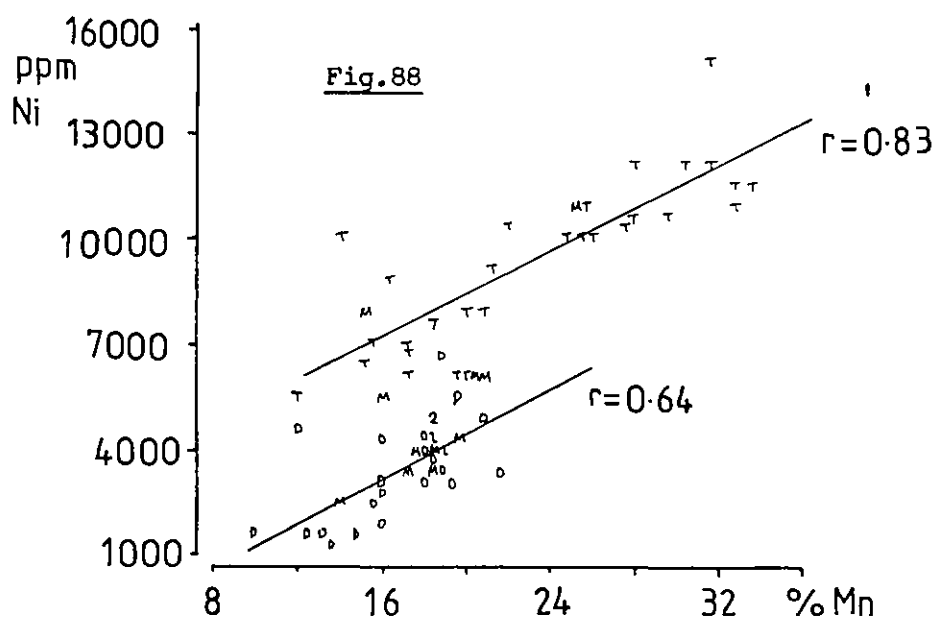
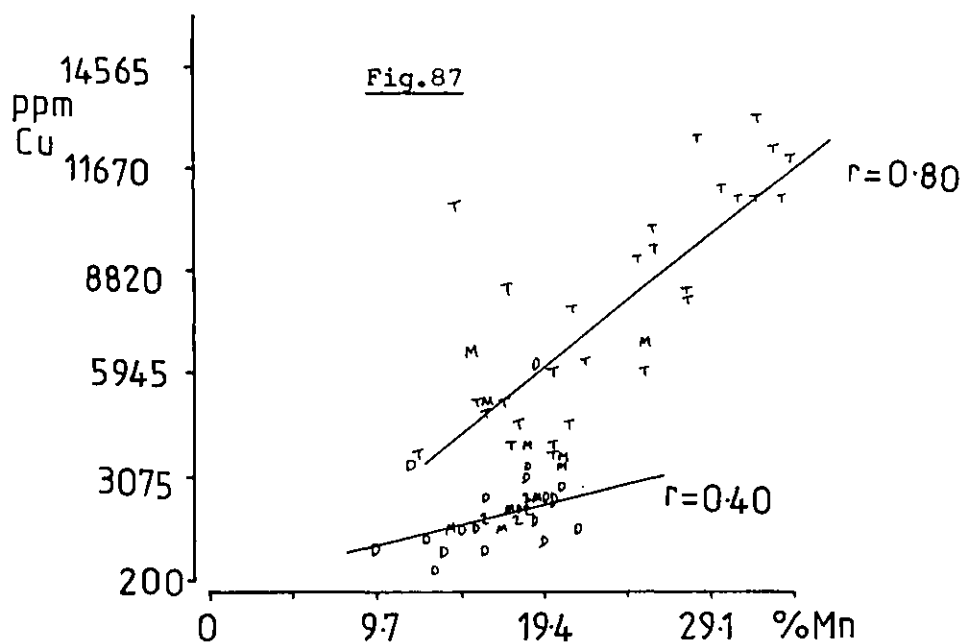
	Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb
Fe	0.07								
Ca	0.54	0.01							
Al	<u>-0.60</u>	<u>-0.63</u>	<u>-0.32</u>						
Ti	0.27	<u>0.78</u>	0.13	-0.56					
Cu	0.40	-0.25	0.38	0.07	-0.14				
Ni	<u>0.65</u>	-0.40	0.45	0.03	-0.13	<u>0.84</u>			
Co	<u>0.75</u>	0.03	0.33	<u>-0.60</u>	0.48	-0.05	0.30		
Pb	0.27	<u>0.79</u>	-0.19	-0.56	<u>0.62</u>	-0.47	-0.40	0.45	
Zn	0.01	0.19	0.35	-0.19	0.50	0.10	0.04	-0.2	0.03

$r(99.9\% \text{ significance level} = 0.60)$

Table 64 Element correlation matrix for Fe-Mn nodules containing todorokite as the dominant Mn oxide mineral. Underlined values are significant at the 0.001 level

	Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb
Fe	<u>-0.77</u>								
Ca	0.37	-0.06							
Al	0.42	0.37	-0.22						
Ti	<u>-0.58</u>	<u>0.68</u>	<u>-0.22</u>	<u>0.71</u>					
Cu	<u>0.81</u>	<u>-0.85</u>	0.30	-0.23	-0.49				
Ni	<u>0.83</u>	<u>-0.82</u>	0.31	-0.34	<u>-0.58</u>	<u>0.88</u>			
Co	-0.23	0.65	0.41	0.37	0.48	-0.42	-0.37		
Pb	-0.49	<u>0.82</u>	0.14	0.31	0.50	-0.67	-0.53	<u>0.83</u>	
Zn	<u>0.90</u>	<u>-0.83</u>	0.18	<u>-0.59</u>	<u>-0.65</u>	<u>0.86</u>	<u>0.79</u>	-0.50	<u>-0.69</u>

N = 28 $r(99.9\%) = 0.58$



Figs.87-89 Cu, Ni, and Zn vs. Mn in S.W. equatorial Pacific nodules. Separate regression lines are for todorokite-rich nodules (T), and for todorokite-poor (M) and δMnO_2 nodules (D) combined. Values of r represent the linear correlation coefficients between the element and Mn in each sample suite.

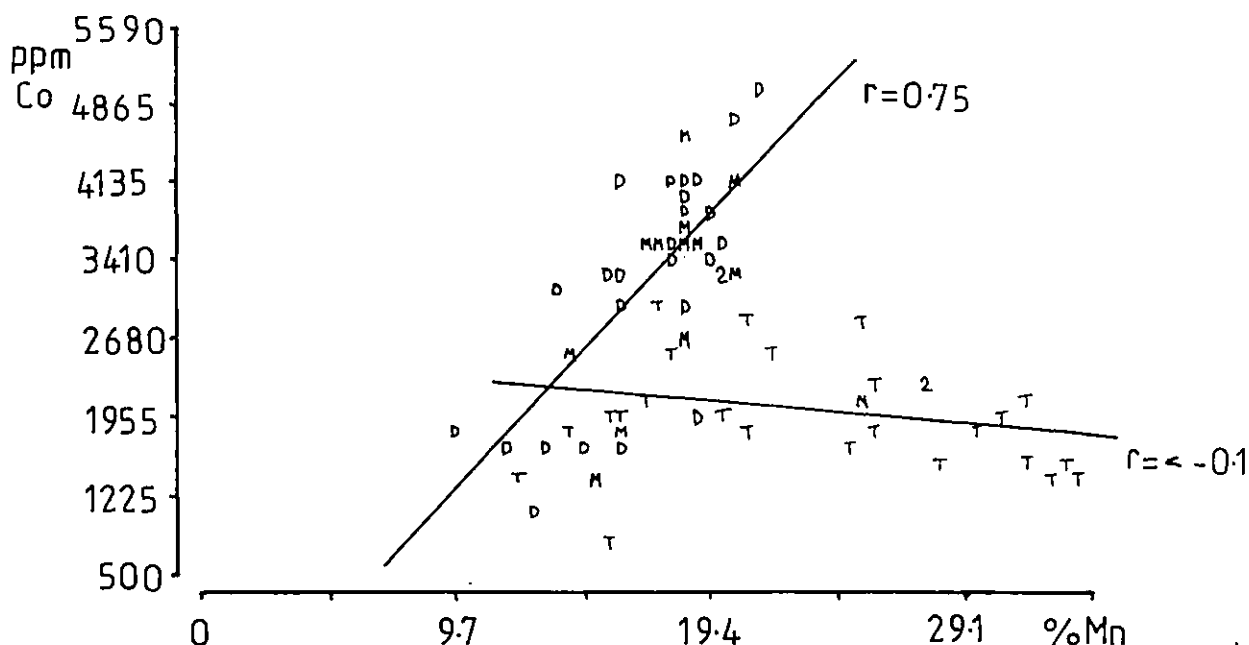


Fig. 90 Co versus Mn in the S.W. Pacific nodules. Separate linear regression lines are for todorokite-rich nodules (T), and for todorokite-poor nodules (M) plus δMnO_2 nodules (D) combined. Values of r represent the linear correlation coefficient between Co and Mn.

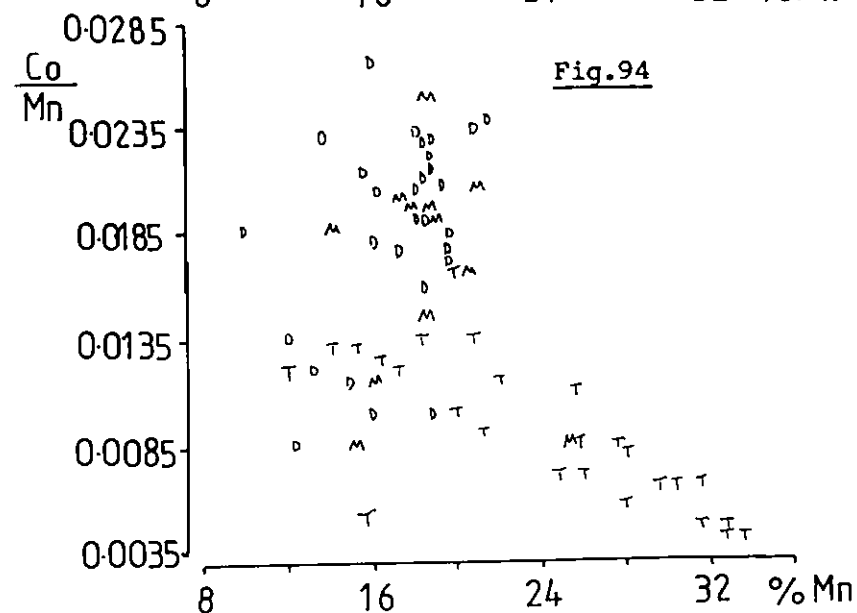
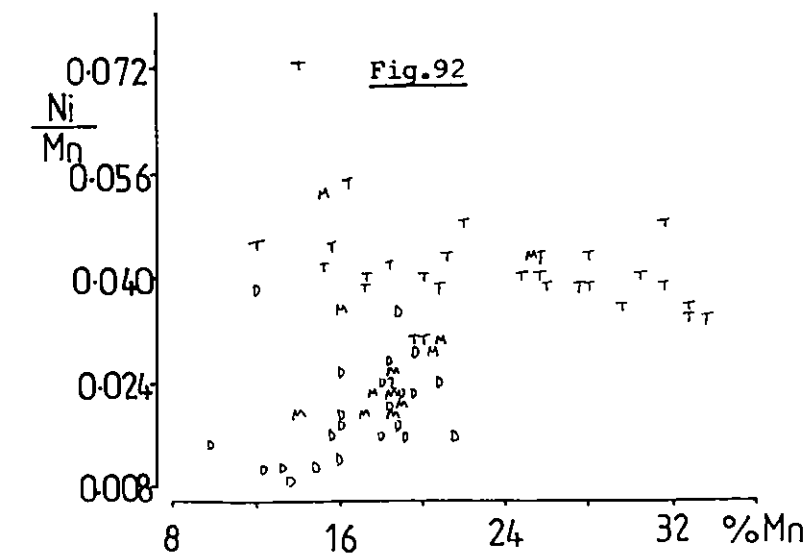
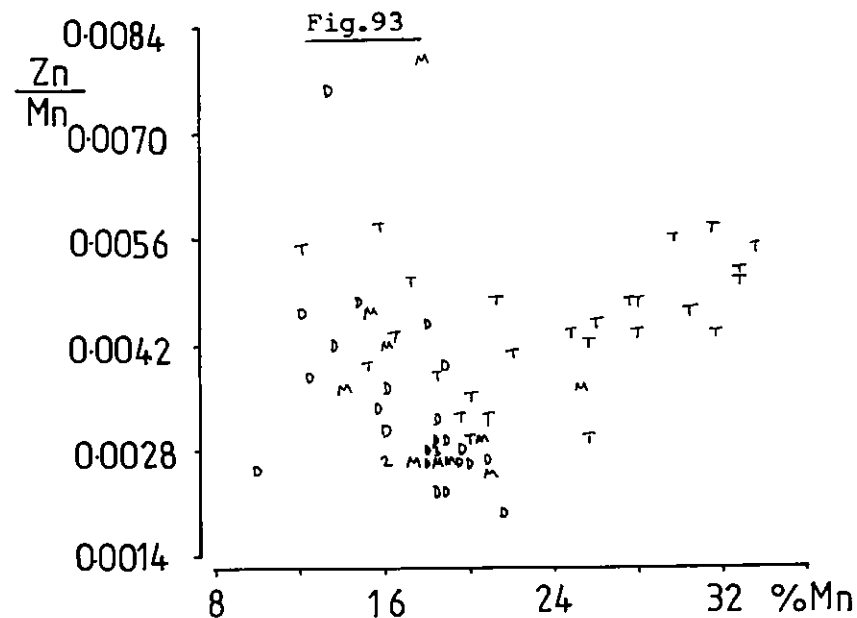
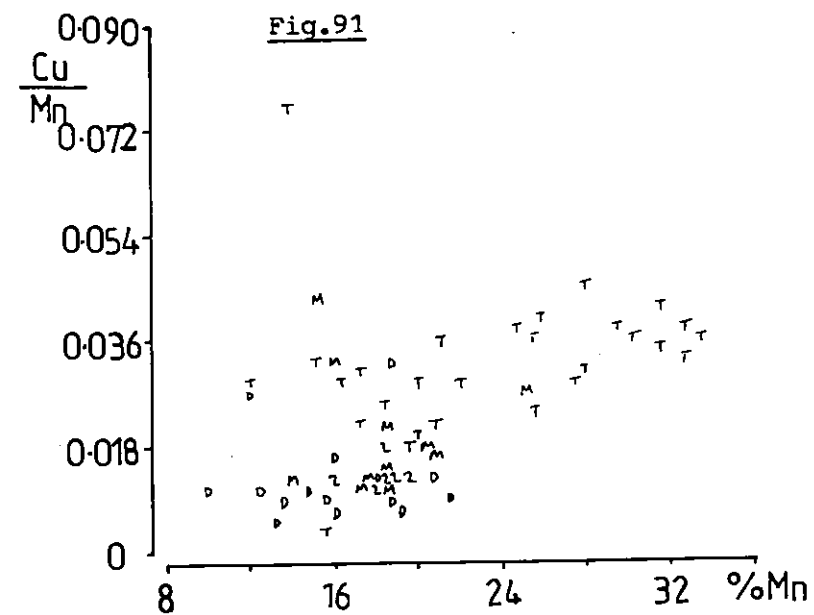
2. Ni is associated with Mn in both mineral groups.
3. Cu and Zn are associated with Mn only in todorokite-rich samples. As in the crusts, poor correlations are seen between Mn, Cu and Zn in the δMnO_2 -nodules.
4. Co appears to be associated with Mn in δMnO_2 -nodules, but with Fe in todorokite-nodules. This observation can explain the confusion over the phase association of Co in nodules, in which Fe-Co and Mn-Co correlations have been reported (e.g. Goldberg 1954, Barnes 1967, Cronan and Tooms 1969).

Halbach et al. (1982) have suggested that the observed Mn-Fe-Co relationships may be due to Co^{2+} adsorption, oxidation and substitution reactions with Mn oxides in hydrogenetic nodules with a similar reaction sequence occurring with Fe hydroxide-silicate particles in diagenetic nodules. The depleted Co content of todorokite is explained by its weaker specific adsorption at the pH range (6.5 - 7.5) at which todorokite is suggested to form, compared to pH 8 for 8MnO_2 formation.

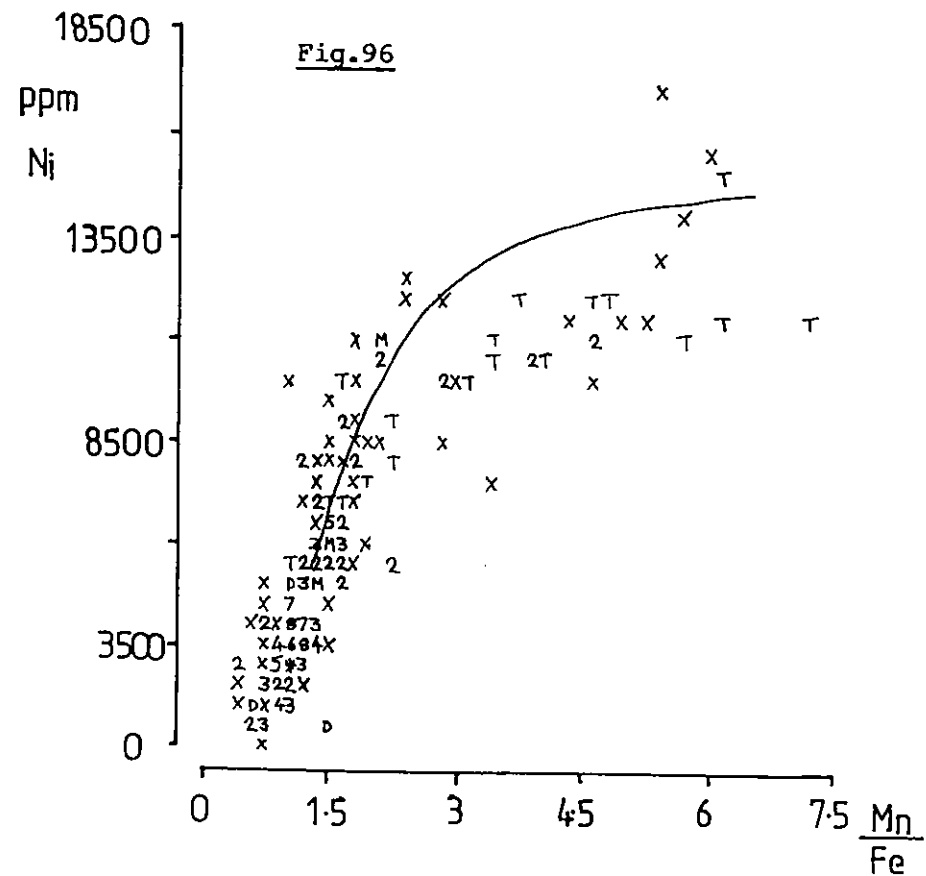
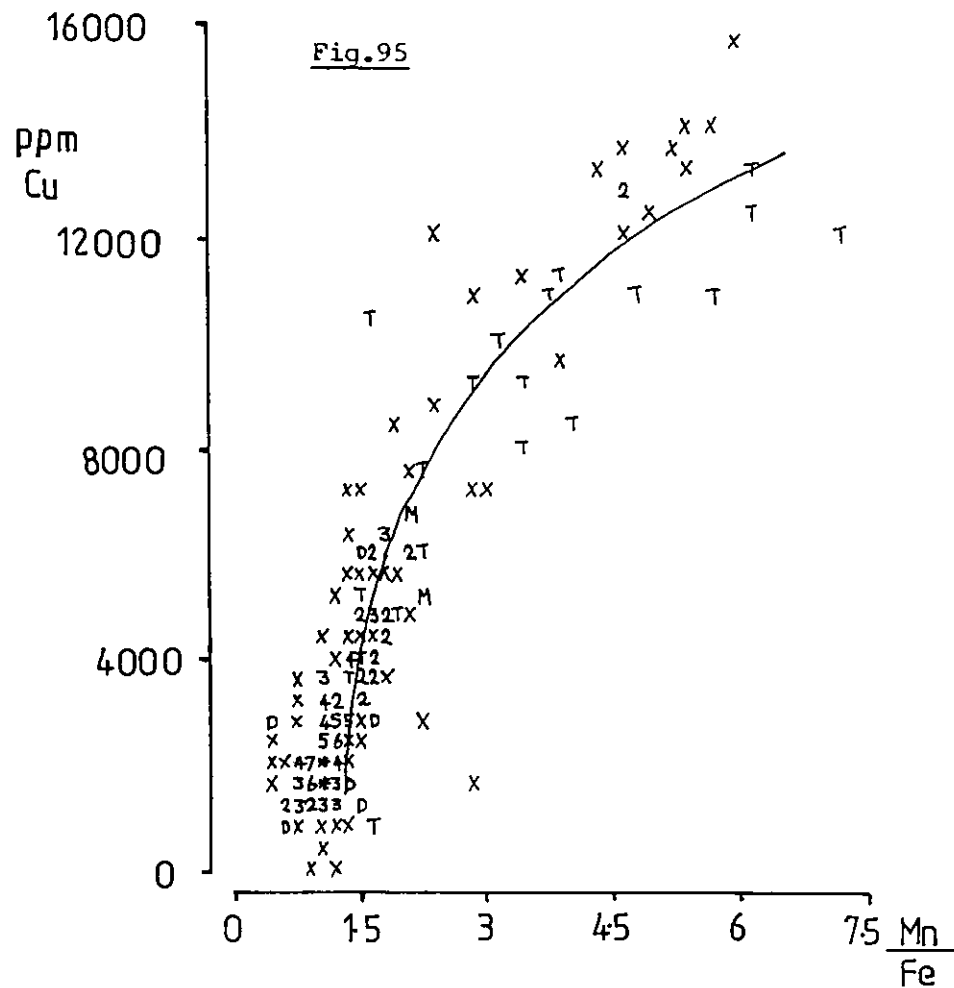
Since the Co-enriched layers of diagenetic nodules contain, on average, more Mn than Fe, there is no need to invoke Fe hydroxide - silicate as the site of Co adsorption and oxidation. Indeed, Co often shows a distinct antipathetic relationship with Fe; for example, exceptionally Fe-rich Atlantic Ocean nodules exhibit very low Co contents (Moorby and Cronan 1981).

A simpler explanation for the Mn-Fe-Co relationships observed in nodules is that most Co in sediments is associated with Mn oxide and is present in the trivalent state, an idea supported by HHA leach data (Section 11.5.2). The positive correlation between Fe and Co and their low abundances in diagenetic nodules results from the relative immobility of both in diagenetic reactions.

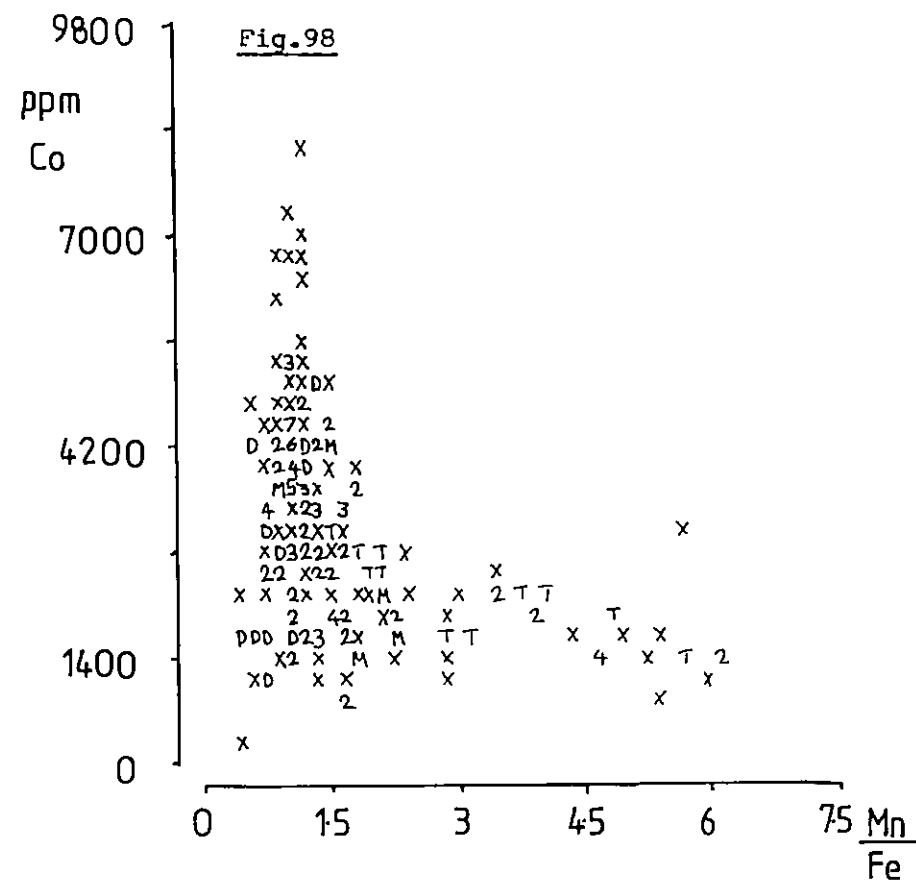
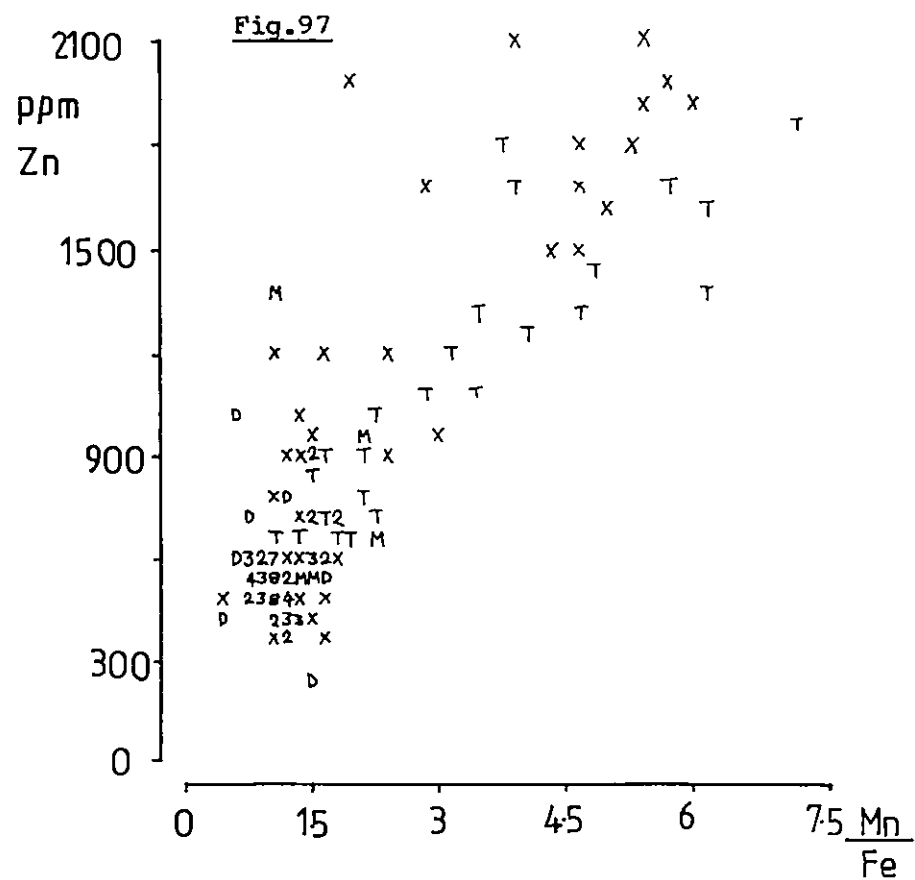
Nodules developing in areas where reductive remobilisation of Mn is an important process show high Mn/Fe ratios and decreasing (Cu + Ni) contents as a result of dilution by an increased supply of Mn. Plotting Cu and Ni versus Mn/Fe for a suite of SEP nodules, Halbach et al. (1981a) observed that Cu and Ni abundances declined at Mn/Fe ratios above 5. In the SWP, the 'point of reversal' is not observed, since Mn/Fe ratios greater than 5 are rare (Figs. 95 and 96). The most striking feature of the SWP plots is that whilst Cu and Zn (Fig. 97) increase with Mn/Fe, Ni is constant at Mn/Fe values greater than 2.5. Whilst the regression line for NEP nodules well defines the Cu:Mn/Fe plot in SWP nodules, SWP nodules are depleted in Ni relative to NEP nodules.



Figs.91-94 Cu/Mn, Ni/Mn, Zn/Mn and Co/Mn ratios plotted against Mn in S.W. equatorial Pacific nodules. Symbols as in Fig.87.



Figs.95+96 Cu, Ni vs. Mn/Fe for S.W. equatorial Pacific nodules. The hyperbolic regression lines for N.E. Pacific nodules are taken from Halbach (1981a). 'x' represents a sample of unknown mineralogy. Other symbols as in Fig.87.



Figs.97+98 Zn,Co vs.Mn/Fe for S.W. equatorial Pacific nodules. Symbols as in Fig.87.

Plots of Co (Fig. 98), Pb and Ti versus Mn/Fe are defined by hyperbolic distributions, with high and variable element contents at ratios between 1 and 2.

12.6 Nodule-crust relationships

The rather constant composition of Fe-Mn crusts forming below 2 km depth along the LIA, both spatially and temporally, suggests that oxide material accumulating directly from the water column has a constant composition. Differences between nodule and crust composition should reflect processes occurring in associated sediments.

Mean element abundances for the crusts, δMnO_2 -rich nodules and todorokite-rich nodules are given in Table 65. Whilst the todorokite nodules show compositions very distinct from the crusts, the similarities between both the chemistry and the mineralogy of the crusts + δMnO_2 nodules suggest they are genetically related deposits. The crusts do however, exhibit higher Mn, Pb and particularly Co contents compared to the δMnO_2 nodules. This suggests that the composition of the 'hydrogenetic' nodule material is affected by reactions in associated sediments.

Table 65 Mean composition of LI crusts dredged from below 2 km, δMnO_2 nodules + todorokite bearing nodules

	LI Crusts		δMnO_2 nodules		Todorokite nodules	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
<u>Element</u>						
Mn	19.5	4.3	16.8	2.9	23.5	6.5
Fe	17.6	3.6	17.3	5.0	8.9	2.4
Cu	0.17	0.09	0.22	0.11	0.76	0.34
Ni	0.36	0.07	0.34	0.14	0.94	0.23
Co	0.47	0.19	0.32	0.11	0.20	0.06
Pb(ppm)	950	440	800	290	420	180
Zn(ppm)	570	120	540	150	1010	490
Ca	2.6		1.9		1.6	0.5
Al	1.56		2.3		2.8	1.3
Ti	1.20	0.31	1.21	0.30	0.49	0.38

12.7 Nodule-sediment hydrogenous fraction relationships

Since nodules contain approximately 90% oxide material, comparison of their composition with the hydrogenous sediment fraction may be a productive approach to studying nodule-sediment inter-relationships. The limited number of similar studies have been rather unsuccessful (Calvert and Price 1977, Calvert et al. 1978, Moorby 1978, Piper et al. 1979, Skornyakova 1979), the most common conclusion being that the sediment hydrogenous fraction (HSF) and hydrogenetic nodules are compositionally similar, but distinct from diagenetic nodules. The inference is that the HSF and hydrogenetic nodules both derive metals directly from the water column. It is possible to test this hypothesis with the LI crusts data.

In the present work, element ratios have been used to examine the chemical relationships in 36 nodule-sediment pairs. For individual pairs, no clear pattern emerges for any chosen ratio. General trends do however emerge when mean element ratios for the LI crusts ($N = 59$), HSFs ($N = 72$), SMnO_2 nodules ($N = 25$) and todorokite nodules ($N = 28$) are compared (Fig. 99).

Differences in the composition of the HSF should reflect variations in element supply and diagenesis. Differences between the HSF and LI crusts should similarly represent the addition of other oxide bearing phases to the sediment and/or subsequent diagenesis. An estimation of the relative importance of each process may be made using the Co/Mn and Co/Fe ratios, which are significantly lower in the HSF than the LI crusts (Fig. 99). In these oxic sediments, it is not possible to invoke the reductive remobilisation of Mn over distances of a decimetre or more as an explanation for this observation. Furthermore, Bonatti et al. (1971) have suggested that Co has a greater post-depositional mobility than Fe, which would enhance the Co/Fe ratio in the HSF relative to that of the LI crusts.

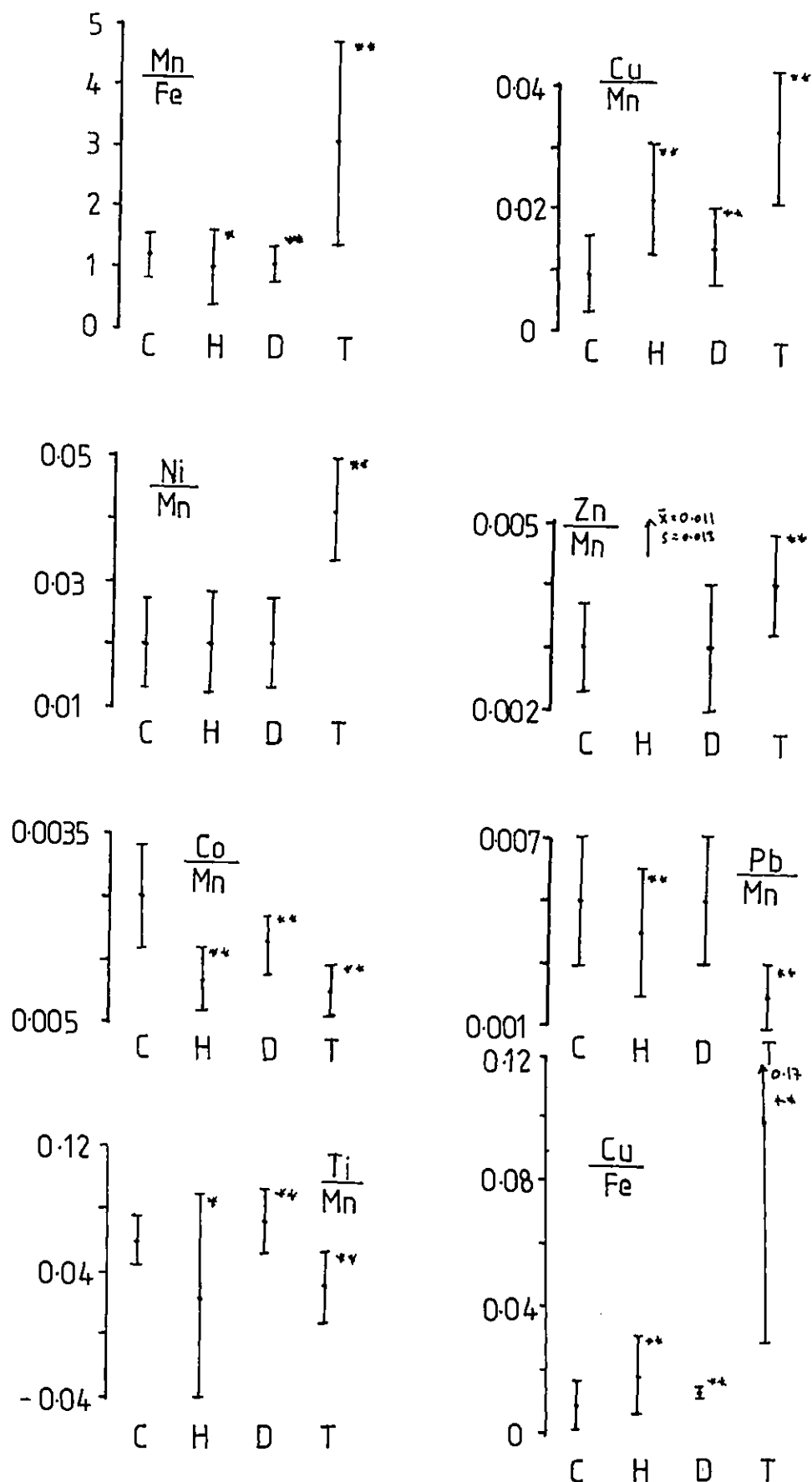


Fig.99 Means and standard deviations of element ratios in the LI crusts(C), the acid-reducible fraction of the sediments(H), δMnO_2 -nodules(D) and todorokite-rich nodules(T). A single asterisk indicates that the samples are derived from populations with a mean different to that of the LI crusts, at the 95% confidence level. Two asterisks indicate the same, but at the 99% confidence level.

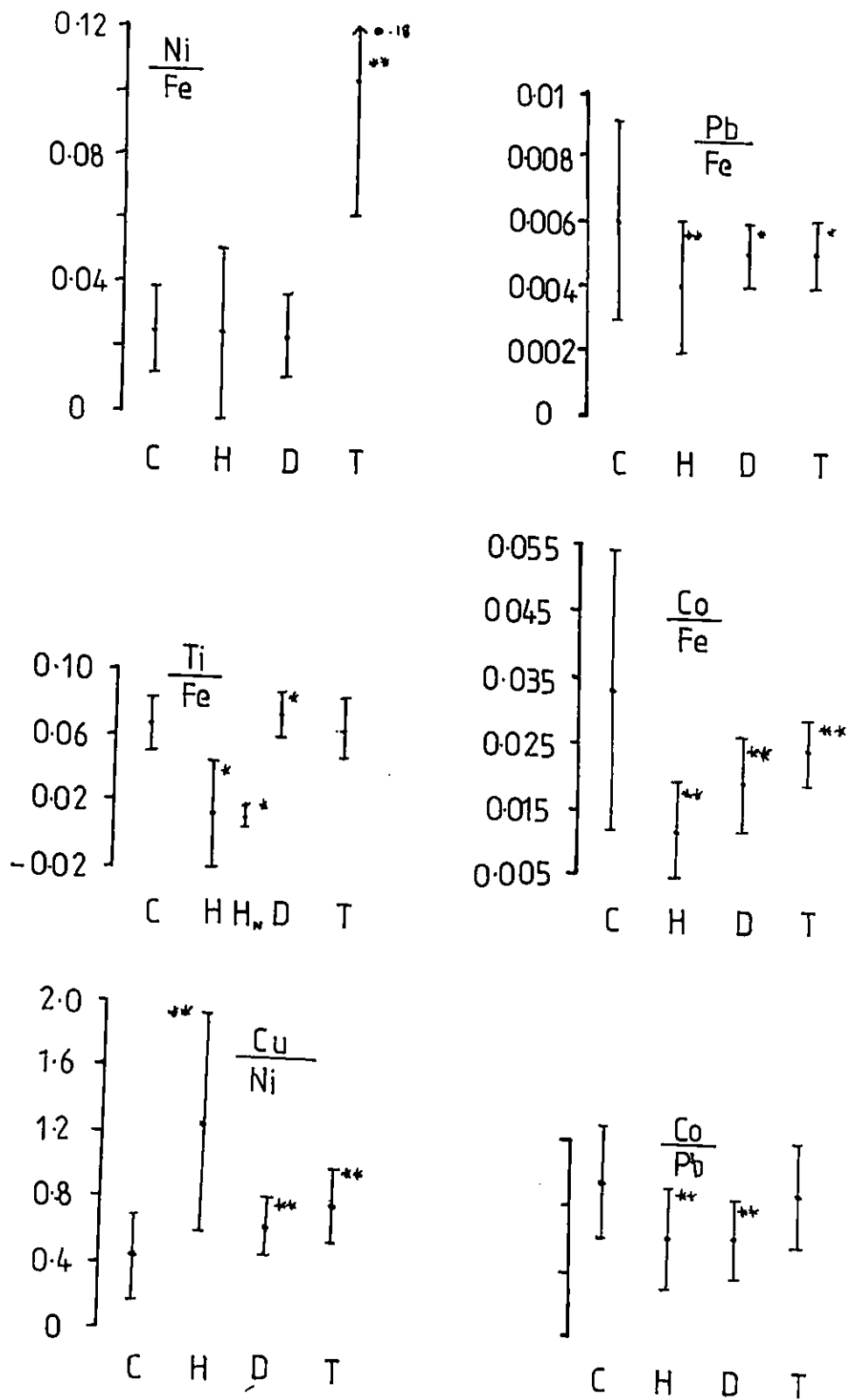


Fig.99(cont.) H_w represents the leachate from the hydroxylamine-hydrochloric-acetic acid attack on some ferromanganese nodules.

Pore water data (Klinkhammer 1980, Hartmann and Müller 1981) suggest that diagenetic reactions may also release metals very close to the sediment-water interface, which can subsequently diffuse into the water column. Since Mn has a greater post-depositional mobility than Co (Bonatti et al. 1971), these reactions may be expected to increase the Co/Mn ratio of the HSF.

From the above discussion it is possible to infer that an Mn-Fe oxide bearing phase is being added to the sediments in addition to that represented by the LI crusts. Comparison of the HSF element ratios with those of the crusts (Fig. 99) suggests that the phase should have a metal enrichment sequence $(\text{Zn}) > \text{Cu} > \text{Mn} > \text{Ni} > \text{Fe} > \text{Pb} > \text{Co}$. Zn is shown in parentheses due to the uncertainties concerning contamination in some samples. This is generally consistent with the metal content of faecal material, which is an important metal carrier phase through the water column (Chapter 9).

SMnO_2 nodules show element ratios between those of the crusts and the HSF (Fig. 99), suggesting that they accrete metals both directly from the water column and from associated sediments. Metals may accrete from sediments either from pore waters or by occluding sedimentary oxide flocs. Mn/Fe ratios of several HSFs and nodules are lower than those of the crusts, suggesting an additional supply of Fe to both. Moreover, there is a positive relationship between the Mn/Fe ratios of SMnO_2 nodules and the associated HSF (Fig. 100). Since Fe is not significantly remobilised in pelagic sediments, the lower Mn/Fe ratios suggest that the direct accumulation of Fe-enriched sedimentary oxides is occurring.

Assuming Fe to be immobile during oxic early diagenesis (Froelich et al. 1979), normalisation of each element to Fe in todorokite-rich (diagenetic) and SMnO_2 -rich (non-diagenetic) nodules yields a measure of its mobility during early diagenesis. As expected, the data suggest that Mn, Cu, Ni and Zn are mobile, whilst Fe, Co, Pb + Ti are not; it is interesting to note that the latter group are removed from seawater in their higher valence states.

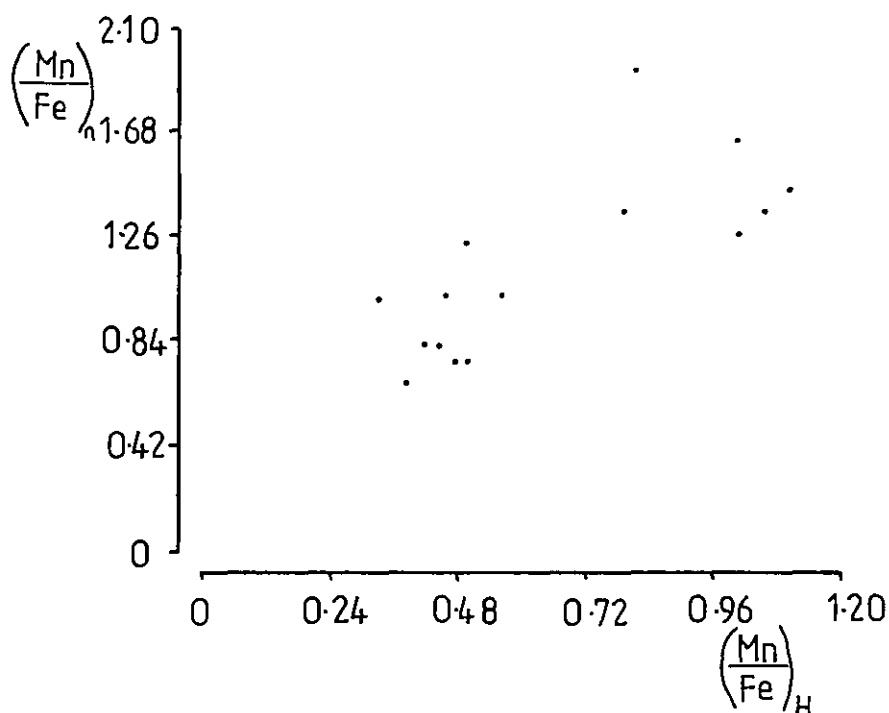


Fig. 100 Plot of the Mn/Fe ratio of SMnO_2 nodules against the Mn/Fe ratio in the acid-reducible fraction of associated sediments.

Within the 'immobile' group of elements, Co is enriched over Fe and Pb in todorokite nodules relative to SMnO_2 nodules (Fig. 99), which may be explained by the weak remobilisation of Co during early diagenesis (Bonatti et al. 1971).

Co^{2+} may enter the todorokite lattice (Giovanoli et al. 1975), or adsorbed Co^{2+} may be oxidised and replace Mn^{4+} in the MnO_6 octahedra, as envisaged for SMnO_2 (Murray and Dillard 1979, Burns, 1976).

12.8 Relationships between nodule composition, depth and sediment lithology

12.8.1 Biogenic Components

Piper and Williamson (1977) have suggested that Pacific nodules with high Mn/Fe ratios and high Cu + Ni concentrations tend to occur in areas where primary

productivity is high and sediment accumulation rate low. Such areas, including the classic NEP, occur on the fringes of high productivity regions close to where the CCD intersects the ocean floor. To take account of these observations, a genetic model for the formation of the high grade nodules has been proposed. According to this, an increased supply of the critical elements Cu, Ni and Zn is envisaged through enhanced dissolution of both carbonate and siliceous tests and their labile fractions below the lysocline (Greenslate et al. 1973, Cronan 1980). Mn may fractionate from Fe either in response to a slight lowering of Eh as organic matter is utilised in the uppermost part of the sediment column (Price and Calvert 1970, Halbach et al. 1981a) and/or by a diagenetic reaction between biogenic silica and Fe-Mn oxyhydroxides (Lyle et al. 1977, Calvert et al. 1978). Such hypotheses imply an association between nodule composition, depth and sediment lithology.

Similar ideas have been used to interpret occurrences of high grade nodules in the south equatorial Pacific. Pautot and Melguen (1979) have shown that the highest nodule grades and abundances in the Tiki and Tapu Basins occur between the sedimentary lysocline and the CCD, partly in response to enhanced dissolution of CaCO_3 by aggressive AABW. In the present study area, Exon (in press) has suggested that nodules are most abundant between 4500 and 5500 m and that the highest grades occur close to the CCD (4800-5000 m).

Hypotheses relating depth, the lysocline and the CCD to nodule grade (and abundance) may be misleading if in a particular area there is no other depth regime against which to test the hypothesis. Thus in the Tiki Basin very little of the seafloor lies below the CCD, whilst in the Penrhyn-Tokelau area little is above the CCD. The most striking fact concerning grade and abundance in both the present and Pautot and Melguen's (1979) work is the great variability in both parameters at any depth. The immediate environment of the nodule would seem to be a more important control on its composition than its depth.

In contrast to the NEP and Bauer Basin, high grade nodules in the SWP are not obviously related to sediments rich in biogenic silica. The most highly siliceous sediments occur in the NW Penrhyn Basin and the Tokelau region, where nodule Mn/Fe ratios are generally around 1 (Figs. 50 + 85).

Unfortunately the abundance of biogenic silica in a sediment is a poor measure of its flux to the sediment surface, both because significant dissolution can occur at the sediment-water interface (Cobler and Dymond 1980) and because other sedimentary components, particularly calcite, may dilute its abundance. Furthermore, calculations of metal fluxes to the sediment-water interface suggest that opal is a carrier phase of secondary importance, particularly for the important elements Cu and Mn.

Similar arguments may be applied to the role of calcite in the formation of high grade nodules. Firstly, carbonate dissolution and the sedimentary lysocline are poorly related phenomena (Section 10.2.2), with abundant dissolution occurring above this level (Berger 1971). Secondly, flux calculations suggest that calcite is an unimportant carrier phase for metals to the sediment surface.

Because CaCO_3 can be an important sediment builder in the pelagic regime (e.g. Hays et al. 1969), it is suggested that the importance of carbonate dissolution to nodule formation lies in the reduction of sedimentation rates to levels at which nodules can form, regardless of their chemistry. In addition, reduction in sedimentation rates may have the effect of concentrating metal rich phases such as faecal material at the sediment-water interface, from which metals may be released and incorporated into nodules.

12.8.2 Volcanogenic components

Murray (Murray and Renard 1891), Arrhenius et al. (1964) + Bonatti and Nayadu (1965) have proposed that volcanism or basalt alteration represents a metal source to nodules. In the present study area sediments with the greatest volcanogenic component occur in the Samoan Passage and to the south east of the Manikiki Plateau (Fig. 53). Fe oxides associated with volcanic glass have been observed in these sediments (Section 10.2.7, Plate 24), which further exhibit particularly low Mn/Fe ratios in the HSF, lower than in the LI crusts (Fig. 85). A halmyrolytic source of Fe may therefore be proposed, in accordance with Hart's (1973) work on the low temperature weathering of basalt. The low Mn/Fe ratios of nodules from the same areas (Fig. 85) and the positive correlation between the Mn/Fe ratios in δMnO_2 nodules and associated sediment HSFs suggests that some of the Fe is also incorporated into the nodules.

The data do not support a halmyrolytic source for other elements. Although Ti appears to be strongly associated with volcanic material in the sediments (Section 11.3), its abundance in hydrogenetic crusts (mean 1.20%) indicates there is no need to infer a volcanic source for Ti, but does not rule out the possibility. The immobility of Ti during basalt weathering (Colman 1982) mitigates against an important halmyrolytic source however.

The partitioning of Ti between co-existing phases in the nodules is of interest since there is a marked discrepancy between the percentage of the total Ti residing in the oxide phases as determined by leaching experiments with HHA (10-20%, Moorby and Cronan 1981) and estimated by correcting for the presence of aluminosilicates (70-90%, Calvert and Price 1977). Arrhenius (1963) similarly found that significant quantities of sedimentary Ti were leachable by HCl but not by HHA, which he interpreted as being due to the leaching by HCl of impure, poorly crystalline rutile.

Table 66 Comparison of quantities of Fe and Ti residing in nodule oxide phases calculated by leaching with HHA and by correcting for aluminosilicate impurities. Fe in weight %. Ti in ppm

Sample	Bulk Fe	HHA leach-able Fe	Alumino- ¹ silicate corrected Fe	% total Fe leachable	% Fe in non Al Si phases	Bulk Ti	HHA leachable Ti	Alumino- ¹ silicate corrected Ti	% total Ti leachable	% Ti in non AlSi phases	(Ti/Fe residue)
K1-2T	11.27	6.86	8.63	61	77	14100	1200	11500	9	82	0.58
K1-4	6.00	3.21	4.3	54	72	5200	800	4900	15	94	0.38
K1-6M	17.60	13.94	16.8	79	95	12000	1300	11300	11	94	0.35
K1-9S	19.30	11.08	18.0	57	93	20000	1500	19800	7	99	0.26
K1-13	12.10	6.36	10.2	53	84	11300	900	10600	8	94	0.25
K2-1	11.75	7.56	8.9	64	76	8900	1300	6100	15	69	0.36
K3-1A	4.64	2.30	3.0	50	65	2600	400	1000	15	38	0.09
V18-283	14.40	10.19	13.06	71	91	12400	1400	10700	11	86	0.32
V18-284	15.20	9.79	13.02	64	86	15000	1100	12800	7	85	0.36

¹ Calculated from the mean element/Al ratio in S.W. Pacific sediments and the Al content of the nodules. 0.5% Al was assumed to be present in non-aluminosilicate phases.

Similar studies on 9 SWP nodules are consistent with these observations, and also show that significant quantities of Fe are present in HHA resistant, non aluminosilicate phase(s) (Table 66). One explanation of these results is that Fe and Ti reside in separate weakly crystalline phases. However, the mean Ti/Fe ratio of the calculated 'phase' is 0.33 ($s = 0.12$), similar to that of the non-crystalline sedimentary phase which is ammonium oxalate-oxalic acid soluble but resistant to HHA (mean = 0.44, $s = 0.14$, see section 11.5.2.3), and much higher than the HHA resistant phase in some North Pacific nodules (mean = 0.09, $s = 0.04$, Bischoff et al. 1981).

The similarity of the Ti/Fe ratios is what may be considered as corresponding phases in sediments and nodules suggests a genetic relationship between the two. Since Fe and Ti are positively correlated in δMnO_2 -rich nodules but not in the LI crusts, Ti and Fe may conjoin during sedimentary early diagenesis, and become occluded into developing nodules.

12.9 Nature of the diagenetic reaction

The importance of sedimentary diagenesis in the development and composition of associated nodules may be seen by comparing the growth rates of diagenetic nodules with hydrogenetic crusts. For the latter, Ku et al. (1982) have measured rates of 1 mm My^{-1} , whilst rates of up to 150 mm My^{-1} have been determined for highly diagenetic SEP nodules (Reyss et al. 1982). Similarly Moore et al. (1981) determined that the top surface of a nodule from the siliceous ooze belt of the NEP was growing at 4.7 mm My^{-1} whilst the bottom surface was growing at 12 mm My^{-1} . Converted to metal accumulation rates, the data show that Mn, Cu, Ni and Zn were accumulating 3-9 times faster on the bottom surfaces of the nodule than the top surface. Further, Piper and Williamson (1977), have found a positive correlation between the Mn/Fe ratio of nodules and their growth rate. It is therefore

suggested that enhanced diagenesis (greater fractionation of Mn from Fe) leads to a greater rate of Mn accumulation in nodules, and also of Cu, Ni and Zn (Lyle 1982).

Lyle et al. (1977) have suggested that Mn may fractionate from Fe in oxic sediments through the reaction of Fe-Mn oxyhydroxides with biogenic silica to form an Fe-rich smectite, releasing Mn which is not accepted in the smectite structure. Whilst clay mineralogical and chemical studies (Section 10.3) suggest that the reaction is regionally important, chemical analyses of the HSF of the sediments give Mn/Fe ratios generally between 0.7 and 1.4, close to that of the hydrogenetic LI crusts. This suggests that the reaction proposed by Lyle et al. (1977) cannot sufficiently fractionate Mn from Fe to explain the Mn/Fe ratios observed in many nodules. Furthermore, areas both where the reaction is deemed to be important (S. Penrhyn Basin) and which contain sediments rich in biogenic silica (Tokelau region) are characterised by nodules which are dominantly hydrogenetic (Table 61, Fig. 85).

The Lyle et al. hypothesis cannot in addition explain the positive correlation between Mn/Fe ratios and growth rates of nodules (Piper and Williamson 1977, Lyle 1982). This is consistent with the classic hypothesis for the enrichment of Mn over Fe in nodules in which Mn is reductively remobilised in poorly oxic sediments (e.g. Price and Calvert 1970).

Most probably, the reduction of Mn is coupled to the oxidation of organic carbon. Sediment trap studies (Bishop et al. 1977, Honjo 1978, Spencer et al. 1978, Deuser and Ross 1980, Wefer et al. 1982) suggest that a rather constant proportion of surface water primary productivity reaches the seafloor. Enhanced remobilisation of Mn and consequently higher nodule Mn/Fe ratios may therefore be expected in regions of high primary productivity. On an ocean-wide scale, this is supported by the close correspondence of the two parameters, except along the axis of the equatorial zone of high productivity

where carbonate sedimentation is occurring (Figs. 101 + 102). Particularly high Mn/Fe ratios are observed in the SEP (Halbach et al. 1980, 1981b) where productivity is in excess of $150 \text{ gC m}^{-2} \text{ y}^{-1}$ and where exceptionally high nodule growth rates have been measured (Reyss et al. 1982).

The SWP data support a diagenetic reaction involving the reductive remobilisation of Mn. The widening of the equatorial high productivity zone eastwards between 175°W and 145°W (Fig. 102) is mirrored by the distribution of todorokite-rich nodules with high Mn/Fe ratios (Figs. 85 and 86).

Calculations by Bender (1971) and Elderfield (1976) suggest that upwards diffusion of reduced Mn is unimportant in enriching surface sediments in Mn in areas, like the SWP, where the SWP oxic layer is thicker than approximately 20 cm. The reductive remobilisation of Mn and other diagenetic reactions which drive nodule growth must therefore occur in the uppermost layers of the sediment column. This is supported by the interstitial water profiles of Cu, Zn, Ni and Mn (Callender and Bowser 1980, Klinkhammer 1980, Hartmann and Müller 1981, Klinkhammer et al. 1982), which typically show Cu and Zn maxima in the upper 2 cm of sediment and Ni and Mn maxima between 5 and 15 cm. These observations are consistent with a model in which Cu and Zn are released from organic phases in surface sediments coupled to reductive dissolution of (Cu-Zn)-Ni bearing Mn oxides slightly deeper in the column.

Recent calculations by Klinkhammer et al. (1982) do however, suggest that upwards diffusion, even on a scale of a few centimetres, cannot supply the Mn and Ni accumulating in diagenetic nodules developing in oxic sediments.

One way of looking at this apparent anomaly is to suggest that nodule growth is a non-steady-state process strongly influenced by microscale diagenetic reactions occurring in organic rich surface (upper 0-1 cm) sediments.

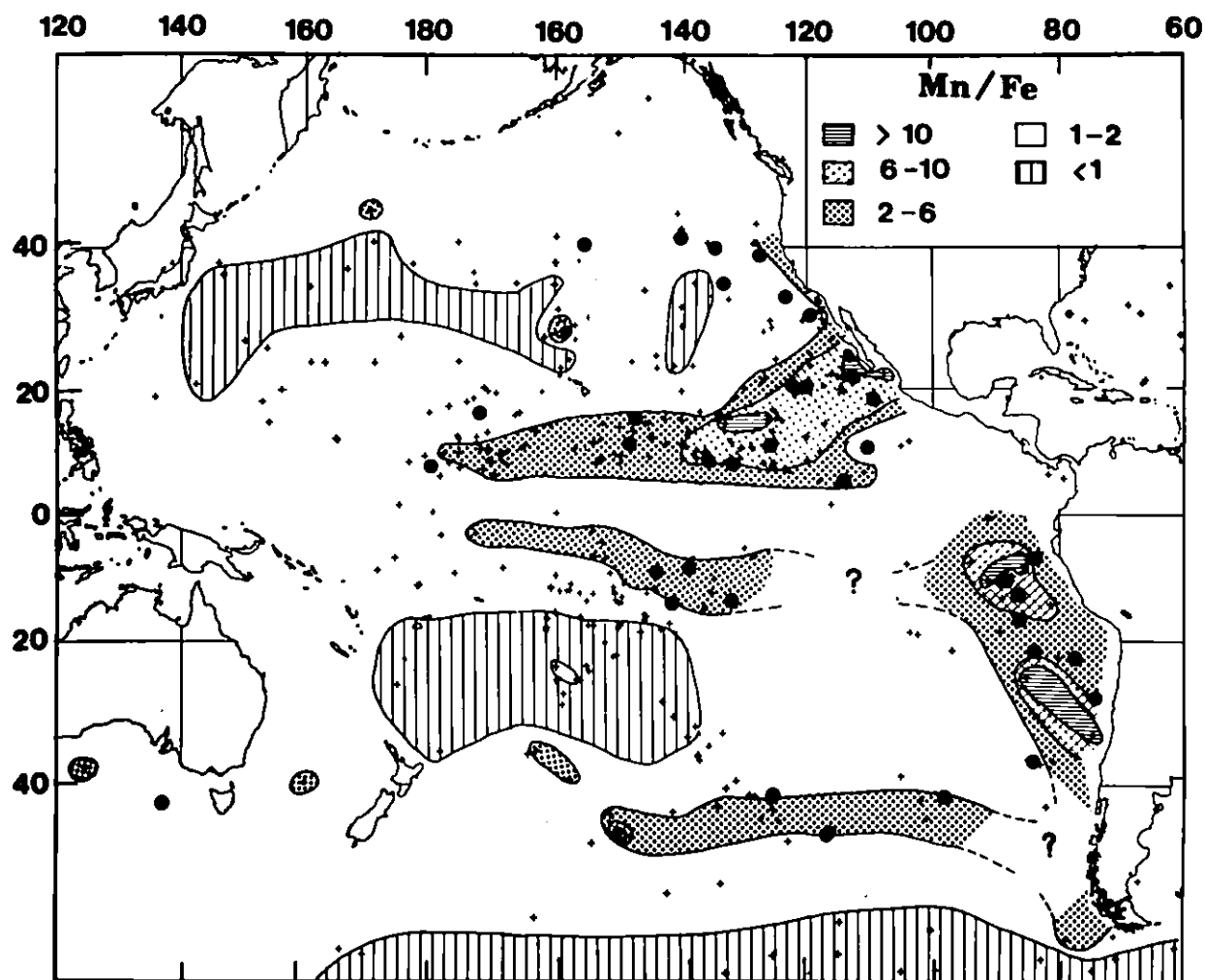


Fig. 101 The distribution of Mn/Fe ratios and todorokite (•) for Pacific Ocean nodules. From Piper and Williamson (1977).

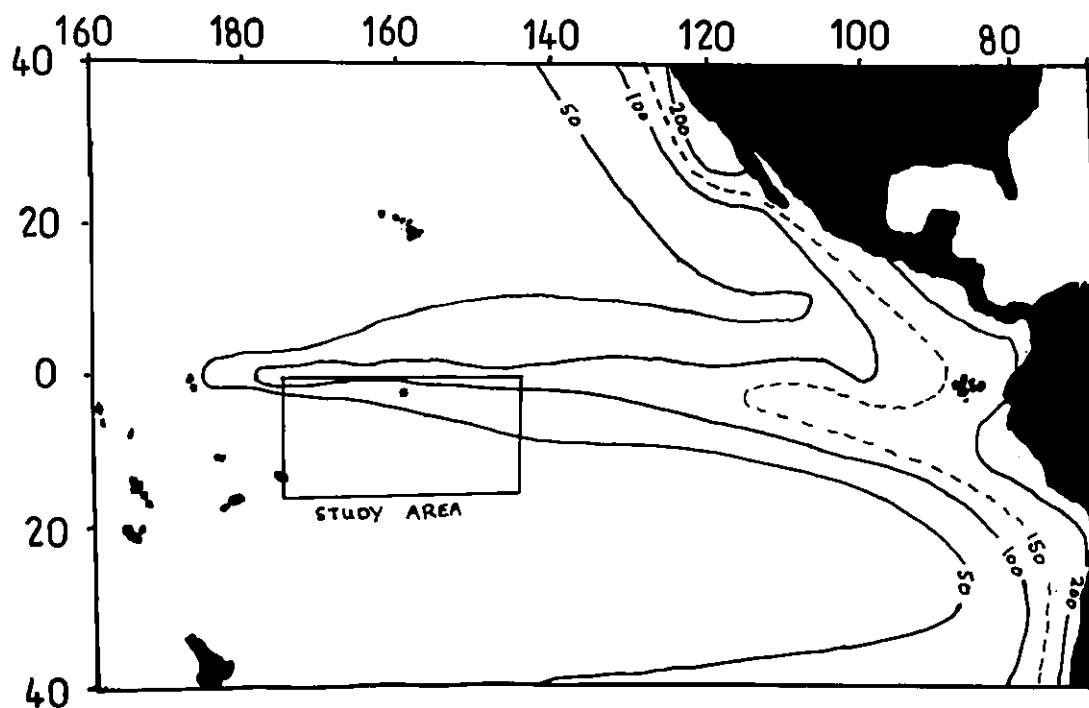


Fig. 102 Isolines of primary productivity in Pacific Ocean surface waters. Units are $\text{gCm}^{-2}\text{y}^{-1}$. After Schmithüsen 1976).

Enrichment of a surface sediment film by organic material has been observed by Soutar et al. (1981).

Faecal material may play an important role in such microscale diagenetic processes. In regions of low sedimentation rates, where ore-grade nodules occur, it is an important carrier of mass, metals and organic carbon to the sediment-water interface (Chapter 9). Wilson (1978) has observed denitrification in N. Atlantic oxic surface sediments and suggests that the process may occur in the faecal pellet microenvironment. Under such conditions remobilisation of Mn and other elements can occur close to the sediment-water interface. Microscale remobilisation is supported by Hartmann's (1979) observation that Mn, Ni and Cu are sometimes depleted in the interiors of probable organic structures (e.g. burrows) in the sediment.

Diagenesis and metal release in the upper few centimetres of sediment strengthens the concept of the sediment-water interface as the optimum position of nodule growth and may explain the characteristic discoidal to sub-rounded shape of ore-grade nodules. Should nodules become buried under regimes of higher productivity and sedimentation rates, spherical diagenetic nodules may form (Halbach et al. 1980, 1981a).

The Cu-Ni-Zn enrichment of diagenetic nodules has generally been ascribed both to an increased supply of biogenically associated metals under areas of high productivity where such nodules form (Greenslate et al. 1973, Lyle 1982), and a mineralogical control (Cronan and Tooms 1969). Pb and Co, which are depleted in diagenetic nodules, are also supplied in greater abundances under regions of enhanced productivity (Chapter 9), suggesting therefore that Cu, Ni and Zn are selectively remobilised over Co and Pb during early diagenesis. The occurrence of the former group in the divalent state means that each may be supplied directly to pore waters upon release from carrier phases. Co and Pb occur in both their upper and lower valence states, suggesting that their reduction is required before they may contribute

significantly to pore waters. Since, for both elements, this may be predicted by classical thermodynamics, it may be that each is poorly remobilised into surface sediments. One possibility is that Co and Pb are re-oxidised on Mn oxides occurring somewhat below the surface sediments. If Co were present significantly in surface sediments in the divalent state, substitution of Co^{2+} into the todorokite lattice (Giovanoli et al. 1975) would be expected to increase its abundance in diagenetic nodules (cf. Halbach et al. 1982).

Plots of Ni and Cu versus Mn/Fe (Figs. 96 + 95) in SWP nodules show that at a given ratio Ni is depleted relative to NEP nodules but that Cu is present in similar abundances. In contrast, SEP nodules are depleted in Cu relative to NEP nodules but have similar Ni contents (Halbach et al. 1981a). Halbach et al. have explained the higher NEP Cu contents by an additional supply of Cu in siliceous tests, which are not abundant in the SEP. The rather low biogenic silica contents of the SWP sediments mitigates against this hypothesis; another possibility is that organic matter, which may be expected to be more abundant in the higher productivity SEP (Fig. 102), effectively competes for available Cu.

The lower Ni contents of the SWP nodules is difficult to explain. Pore water data (Klinkhammer 1980, Klinkhammer et al. 1982) suggests that whilst significant quantities of Ni is released during the dissolution of Mn oxides in sub-oxic sediments, upwards diffusion can supply some, but not all the Ni accumulating in associated nodules. In the SWP, therefore, it is possible that the Ni/Mn ratio of oxides accumulating directly from the water column is lower than in the NEP, or that Ni is accumulating less rapidly in the important organic-rich surface sediment.

Why does the diagenetic precipitate comprise todorokite? Burns and Burns (1975) have proposed that 5MnO_2 rather than todorokite occurs in nodules in which the Mn/Fe ratio approaches unity since 5MnO_2 and $\text{FeOOH} \cdot \text{H}_2\text{O}$ may epitaxially intergrow and physically hinder the development of the todorokite structure. Recent studies

of Fe-Mn encrustations (Craig et al. 1982; this work) have however shown that deposits with Mn/Fe ratios up to 4.0 exhibit a $8\text{MnO}_2 - \text{FeOOH} \cdot \text{H}_2\text{O}$ mineralogy. Rather, an adequate supply of the divalent cations essential to the todorokite structure (i.e. Mn^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+}) would seem to be the most important prerequisite in its formation.

This problem is complicated by the recognition that even in areas of low productivity elements are supplied to the sediment-water interface in sufficient abundances to account for their accumulation rates in diagenetic nodules (Callender and Bowser 1980, this work). The crucial point may therefore be the degree of remobilisation, which will increase with biological productivity and to a lesser extent with particulate dissolution. Todorokite can form where there is an enhanced supply of Cu^{2+} , Ni^{2+} , Zn^{2+} or Mn^{2+} . In the case of Mn, the rate of supply may be of particular importance, since the rate determining step in the oxidation of Mn(II) to Mn(IV) is its actual oxidation once adsorbed on MnO_2 (Morgan 1964).

The nature of the diagenetic reactions which enhance the Mn/Fe ratios of nodules are such that nodules underlying the axis of the equatorial zone of high productivity may be expected to exhibit high Mn/Fe ratios, whilst in fact ratios are commonly close to unity (Piper and Williamson 1977). Possible explanations of this anomaly are that:-

1. Since nodules are infrequently observed on carbonate sediments, those that do may occur in uncommon situations, for example where sedimentation rates are lowered through winnowing +/- slumping. In such situations nodules may lie on the sediment and grow dominantly within the water column.
2. Calcite acts as a diluent of more metal-rich phase such as faecal material. Metal concentrations and fluxes may therefore be greater at the sediment-water interface of non-carbonate sediments than of carbonate sediments. By this interpretation, the importance of

the sedimentary lysocline is that it marks a level below which sedimentation rates become sufficiently low to concentrate the metal rich phases at the sediment-water interface.

Chapter 13 Summary and Conclusions

This thesis comprises two closely related studies concerning the chemistry of ferromanganese oxide deposits in the equatorial S.W. Pacific. First, a well-controlled suite of ferromanganese encrustations from the Line Islands Archipelago has provided the opportunity to study the hydrogenous end-member of the marine ferromanganese oxide continuum. Second, a suite of nodules and closely associated sediments from basinal areas adjacent to the LIA have been examined. This area is situated on the edge of the equatorial zone of high productivity and is thus in an analogous position to the ore-grade nodule belt of the N.E. equatorial Pacific. In particular, an analysis of the roles of element supply and diagenesis as controls on nodule and sediment acid-reducible fraction chemistry and mineralogy has been made with the recognition that the crusts represent oxide material accreting directly from the water column.

The LI crusts are typically less than 3 cm thick and have formed upon stable substrates of francolite, phillipsite/smectite or intact basalt. Compared to nodules they exhibit a uniform morphology, exhibiting only indistinct layering on a centimetre scale.

Correlation analysis on crusts uncontaminated by detrital minerals has shown that the strongest associations exist between Mn oxides and a range of trace elements. Particularly strong associations were seen between Mn, Co and Mo, and to a lesser extent between Mn, Cd, Ni, Zn and Pb. Weak associations exist between Fe, Be, Ba, Cu and Al, whilst V, Sr, Ag and Ti are authigenic elements apparently partitioned between both oxide phases, or in the case of Ti, perhaps as an independent phase.

An analysis of variance procedure has indicated that much of the chemical variability in the crusts is depth related. Below 2 km, the composition of the crusts is strikingly uniform in both space and time, and Mn/Fe ratios are between 1 and 1.2.

Crusts of distinct composition occur between 1 and 2 km depth. They have higher Mn contents, exhibit higher Mn/Fe ratios (up to 2.3) and have greater abundances of manganophile elements. Crusts with high Mn/Fe ratios occur in that part of the water column in which there is a dissolved Mn maximum associated with the oxygen minimum. The 'excess' Mn, derived from the oxidative decay of organic material, is scavenged and oxidised by pre-existing oxide flocs. This process of 'adsorption and occlusion' increases not only the Mn/Fe ratio of the crusts, but also their (manganophile element)/Mn ratios.

Mineralogically, the oxide phases of both the LI and Hawaiian crusts (Craig et al. 1982) are comprised almost exclusively of SMnO_2 and $\text{FeOOH}\cdot\text{H}_2\text{O}$, even in samples in which Mn/Fe ratios rise to 4.0. From this it is inferred that the most important pre-requisite for the formation of todorokite over SMnO_2 is not the Mn/Fe ratio of the deposit but an adequate supply of the divalent cations Mn^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} which are essential to the todorokite structure.

As for the transition elements, the REE geochemistry of the crusts shows a dichotomy between samples from 1-2 km and deeper than 2 km. Apart from Ce, which exhibits large and variable positive anomalies, the shallower crusts are depleted relative to the deeper crusts in light and intermediate REE, whilst the abundances of the heavy REE are similar. This is attributed to differential scavenging of REE by Mn and Fe oxides; heavy REE are scavenged equally effectively by Mn and Fe oxides, whilst light and intermediate REEs are more specifically associated with Fe oxides.

Ce is thought to become fractionated from the other REE by its removal from seawater in the higher (IV) valence state, as are Co (III), Ti (IV) and Pb (IV). The common bond between these elements is not however, reflected in their abundances in the crusts, which are not related. Apparently, different enrichment processes are operative for each element.

Overall, it is envisaged that the crusts develop by the accumulation of trace metal enriched oxide flocs from the water column, although the precise mechanisms of enrichment are very much open to question. The cation contents of the crusts are well in excess of the probable electrostatic adsorption capacities of the individual oxides. Whilst the similarity of laboratory determined element selectivity sequences of Mn and Fe oxides and the metal enrichment sequence of the crusts are strikingly similar and serve to stress the importance of specific processes, the precise mechanisms are unknown.

The suite of nodules and associated sediments from 0-15°S, 145-175°W has been regarded as part of chemical sedimentary systems in which material - a fraction of which has a similar composition to the crusts - is supplied to the sediment-water interface and may be removed, remobilised and redistributed to a variable extent by early diagenetic reactions.

The physical environment of the deposits was examined through the use of sediment smear slides and by semi-quantitative analysis of less than 2 μ m clay fractions. The principal conclusions of the smear slide work are that:-

1. most of the region is situated below the CCD,
2. biogenic silica is essentially absent from sediments south of 10°S and rises to maximum abundances of 10-20% in the equatorial north-west of the region,
3. the distribution of volcanic glass suggests that the volcanic components of the sediments is greatest in the Samoan Passage, the Tokelau region and in the immediate vicinity of the Manihiki Plateau, declining towards the east of the region,
4. the zeolite phillipsite is a regionally important sediment component, comprising up to 50% of the bulk sediment in the east of the area. Its distribution, similar to that of fish debris but at variance with that of volcanic glass, indicates that its abundance in surface sediments is related to sedimentation rates and not to a supply of volcanic debris,

5. the oxide fraction of the sediments is composed mainly of extremely fine-grained dispersed material, and coated grains. An Fe oxide source from the weathering of volcanic glass is apparent.

Semi-quantitative clay mineralogy has indicated that smectite comprises 50-90% of the clay mineral assemblage. Similar to phillipsite, smectite shows an antipathetic relationship to volcanic glass and is most abundant in what are considered to be the most slowly accumulating sediments. Combined chemical analysis and scanning electron microscopy suggests that the smectite is an Fe-rich montmorillonite formed predominantly through the combination of Fe oxyhydroxides with biogenic silica. Smectite thus occurs in greatest abundance on those slowly accumulating sediments in which the diagenetic reaction is most enhanced.

Chemical analyses of the sediments have suggested that there is no direct hydrothermal influence in the area. Mn and the associated trace metals Cu, Ni, Co and Pb are, however, enriched with respect to mean Pacific pelagic clay, reflecting the extremely low sedimentation rates in the region. Whilst most of the Mn, Co and Ni is contained within sediment acid-reducible phases, between 25 and 40% of the total Cu, Pb and Zn is associated with smectites.

The calculation of a series of mean element ratios for the LI crusts, the sediment HSFs, δMnO_2 -rich nodules and todorokite-rich nodules has suggested that the first three are compositionally similar and thus genetically related whilst the diagenetic nodules are of very different chemical character. However, subtle differences between crusts, δMnO_2 nodules and sediment HSFs do occur; those between the crusts and the sediments are ascribed to processes of element supply rather than diagenesis, whilst the δMnO_2 nodules appear to represent a mixture of crust-type material and sedimentary oxides. Compared to the crusts, both the sediment HSFs and the δMnO_2 nodules are enriched in Fe relative to Mn. Since Fe is immobile during oxic early diagenesis, it is considered that the component

of the hydrogenetic nodule derived from the associated sediment comprises at least partly occluded Fe(-Mn) oxides.

Since those nodules in the study area with the lowest Mn/Fe ratios are associated with sediments containing an important volcanic component, a halmyrolytic source of Fe to the nodules is inferred. There is no need to infer a halmyrolytic source for any of the other elements examined in this study, although there is some evidence from selective leach data of both sediments and associated nodules that Ti may be supplied in this way, in the form of a Fe-Ti oxide.

The early diagenetic reaction essential to the formation of todorokite-rich nodules appears to be related to the reductive remobilisation of Mn. This is the only diagenetic process consistent with the degree of fractionation of Mn from Fe found in the nodules and observed relationships between nodule growth rates and Mn/Fe ratios (Piper and Williamson 1977, Lyle 1982). Since Mn reduction is likely to be coupled to the oxidation of organic carbon, and since a rather constant proportion of primary productivity reaches the ocean floor, reductive remobilisation is enhanced in high productivity zones. This is observed both in the S.W. Pacific, where the equatorial band of diagenetic nodules contracts westwards parallel to the productivity isolines, and in the Pacific as a whole.

Since pore water data (Klinkhammer et al. 1982) suggests that upwards diffusion even in the upper 2 cm of sediment cannot supply adequate Mn or Ni to account for their accumulation rates in diagenetic nodules, the important reductive processes are likely to occur in a very thin organic-rich surficial sediment layer. Element flux calculations have suggested that in regions of low sedimentation rates faecal material, perhaps aggregated into marine snow, may well be a very important vertical carrier of metals. Assuming that 75% of vertical mass flux comprises material which has passed through organisms'

guts, then the faecal fluxes of Mn, Fe, Cu, Pb, Co, Ti and Al are 1-3 orders of magnitude greater than those with siliceous or calcitic tests and their associated soft parts. The material thus represents an intimate mixture of oxides and labile organic debris, and the degree of Mn remobilisation will depend on the supply rate of organic carbon.

An additional, though smaller, supply of Fe, Cu, Ni and Zn from dissolving biogenic opal may also be envisaged, whilst the supply of trace elements associated with calcite is unimportant. The importance of carbonate dissolution probably lies in the resulting concentration of the oxide-organic-enriched phases at the critical sediment-water interface.

Finally, it should be pointed out that even in regions of low biological productivity there is a sufficient supply of the key elements Mn, Ni and Cu to account for their accumulation rates in diagenetic nodules. The importance of the supply of labile material to the sediment, and the reaction of these phases leading to the redistribution and remobilisation of elements in surface sediments, is thus stressed.

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Appendices

1. Preliminary dredge descriptions from the University of Hawaii 1979 cruise to the Line Islands Archipelago.
2. Classification of the S.W. equatorial Pacific sediments and their major components.
3. Chemical analytical techniques.
4. Data.

Appendix 1

Dredge No.	Sample	Position	Water Depth(m)	Rock Characteristics (from prelim. dredge reports)	Crust thickness (mm)	Substrate Description
041	1/1	2°5.5'N 157°20.6'W	1350- 1550	Volcanic breccia fragments. Enclosed basalt fragments are clinopyroxene-plagioclase-olivine-altered olivine phyrlic set in glassy to holocrystalline matrix with 1-3 mm Mn crust.	5	Vesicular basalt; colour from light rust to dark green. Fine grained.
044	2/2	7°35.3'S 151°32.6'W	1880- 2100	(a) massive, non-vesicular brownish grey basalt. (b) breccia-reddish-brown, angular clasts of basalt in a sandy matrix. Patchy Mn crust. (c) 4 cm thick Mn encrusted fine-grained yellow to reddish-brown breccia.	4	
045	6/13	9°3.7'S 150°41.6'W	1300- 1450	(a) basalt-massive, non-vesicular, olivine phyrlic altered fragments. (b) volcanic breccia- 10 cm long basalt clasts in altered glass matrix. 1-5 cm Mn crust. (c) Limestone + limestone breccia-main rock recovered. (d) Biogenic volcanic sandstone - foram., volcanic debris rich. Oysters, molluscs, echinoid + coral fragments. Late Cretaceous - early Eocene.	20-25	0-5 mm honeycomb of smectite with phillipsite and francolite infilling. Infilling is red - fawn coloured. Some calcite filled vugs.
050	4/6	11°03.1'S 152°05.28'W	4250- 4400	Volcanoclastic sandstone - several angular, Mn-crusts (1mm - 10mm), graded sandstone containing bands of opaques, glass shards, olivine and plagioclase grains and some poorly preserved radiolarians and forams.	30	Rust-coloured, needle-like particles of phillipsite. Some smectite. Black oxide specks
051	2/7	12°52.5'S 150°45.8'W	3000- 3200	Volcanic breccia - 20 cm long basalt clasts in a clay - carbonate matrix; abundant early - late Eocene planktonic forams.	2	Honeycomb of smectite infilled with redder phillipsite matrix. Penetration of Fe-Mn oxide in mm sized lumps.
	3/7				12	Highly altered, pale brown, with redder patches + black specks. Many small (0.25mm) cavities. Phillipsite + smectite.
	5/7				30	Dominantly grey, highly altered friable material, vesicles infilled with rust coloured phillipsite.
	6/7				15	V. pale brown, powdery; oxide penetration.

Appendix 1 (Cont.)

Dredge	Sample	Position	Water Depth (m)	Rock Characteristics (from prelim. dredge reports)	Crust thickness (mm)	Substrate Description
052	4/7	15°00.8'S 149°02.3'W	3400	(a) Basalt - angular to subangular, Vesicular (15%), pillow fragments with glassy chill margin on a few pieces. (b) Volcanic sandstone-graded tuff boulder with interstitial clay.	1	Highly altered yellow volcanic sandstone with 1 mm basaltic (?) grains. Some indurated clay.
053	1/1	13°01.5'S 147°55.7'W	4700	1-20 cm long tabular Mn crusts with pockets infilled with dark brown radiolarian clay. Middle Pliocene - Recent.	6	Dull, smooth upper surface, brown-black in colour. Worm tubes. Undulating. Rough + pitted lower surface. Abundant worm tubes. Brown staining. Crust or substrate? No distinction.
054	1/1	3°38.4'N 159°31.4'W	2800	Mixture of massive, non-vesicular basalts + vesicular (30-40%) lavas. Thin (<1 cm) + patchy crusts.	3	Weathered exterior with hard, volcanic interior.
055	3/3	4°22.3'N 159°05.3'W	2150- 2650	(a) Large chalky limestone boulder. (b) Fine-grained volcanic sandstone fragment with pelecypod burrows. (c) Grey mud balls.	2	Friable chalky; penetration of oxides through pores.
058	1/2	10°48.8'N 165°32.6'W	1150- 1325	Volcanic breccias - angular fragments (5-15 cm long) with small clasts (<1 cm) of sandstone + basalt pebbles set in a pale green clay-rich matrix; Mn coating thin (<1 cm) + patchy.	10	Red-brown with light brown areas (2x2 mm) Calcite (?) vein. Several large (7x7 mm) dark, rounded fragments (basalt?). Some penetration by oxides. Friable once broken up.
	2/2				30	Green; lamina, as in shale. Abraded worm tubes.
059	7/7	12°31.0'N 167°3.3'W	3000- 3750	(a) Basalts-sub-angular 5-25 cm fragments of 10-25% vesicular basalt + massive Mn-free basalts. (b) Angular volcanic sandstones (5-30 cm long) with thin (2 cm) + patchy Mn coating.	5	(1) Vesicular, extremely friable, Fe-stained. Small (1 mm) white spheroids. (2) Agglomerate of well rounded pink + light-brown pebbles (1-2 mm) in a grey matrix. Oxide penetration.
060	2/4	13°27.7'N 165°25.1'W	3850	(a) Basalts - angular to sub-rounded pillow + other fragments (5-20 cm long) of vesicular (<10%) + massive (<10%) basalts with thin (<1 cm) Mn coating. (b) Volcanic sandstone - contain small (1 cm) reddish-brown basalt clasts in an off-white clay-rich matrix.	20	Weathered grey-green volcanic, with 0.5 mm vesicles infilled with white/light brown sediment. Thin coating of light brown sediment.

Appendix 1

Dredge No.	Sample	Position	Water Depth (m)	Rock Characteristics (from prelim. dredge reports)	Crust thickness (mm)	Substrate Description
O60	3/4	13°27.7'N 156°25.1'W	3850		8	Honeycomb of hard fawn-coloured material, infilled with rust-coloured friable material. Fawn specks in the matrix.
O60	4/4				13	As O60 3/4. Honeycomb approximately 0.5 cm diameter.
O61	2/5 (1)	14°58.9'N	2800	(a) Volcanic sandstones - rounded to angular fragments (2-20 cm) with <2 cm patchy Mn coating. (b) Basalts - 5-15% vesicular, angular to sub-rounded pillow fragments (2-20 cm long) with thin (<1 cm) patchy Mn coating.	20	White sand - size grains, plus some 1/2 cm fawn coloured clasts. Oxide penetration; Fe staining.
O61	2/5 (2)				15	Breccia of fine white/yellow friable material and large fawn pebbles (3 cm). Much penetration by oxides. Fe staining.
O61	4/5				30	Mixture of white, indurated sediment + fawn honeycomb infilled with Fe-stained granular material.
O62	1/3	15°09.4'N 168°06.1'W	2700	(a) Basalts-altered, massive (<10%) angular 5-20 cm long fragments, rounded by 2-6 cm Mn coating. (b) Volcanic sandstones - angular 5-20 cm long fragments; 2-6 cm Mn coating.	70	
O62	3/3				65x60	Nodular; core of clay + 3 mm pebbles of unaltered material. Heavy oxide penetration.
O63	1/9	16°26.1'N 168°08.8'W	2325	(a) Basalts - angular 5-20 cm fragments of vesicular (10%) basalt with 1-6 cm Mn coating. (b) Volcanic sandstones - angular, 1-6 cm Mn coating. (c) Limestone - 5-20 cm angular fragments with 2 cm patchy Mn coating.	10	Grey, powdery, clayey matrix surrounding sand-sized white grains. Light brown sediment coating.
O63	2/9				25	
O63	5/9				2	Limestone, speckled with black oxide. Borings, both surficial and at depth, oxide-filled.
O63	6/9A				20	Oxide-penetrated white material; orange + red oxide staining.

Appendix 1

Dredge No.	Sample	Position	Water Depth(m)	Rock Characteristics (from prelim. dredge reports)	Crust thickness (mm)	Substrate Description
O63	6/9B	16°26.1'N 168°08.8'W	2325		5	3-5 mm pebbles (altered volcanic), white cement matrix.
O63	8/9				20	Firm, white, fine grained. Rust-coloured Fe-staining; abundant penetration by Mn+Fe oxides, both in pores and along fracture planes.
O64	2/7	16°25.9'N 168°08.8'W	2400	(a) Basalts - severely altered + heavily (1-3 cm) Mn coated. (b) Volcanic sandstones - 2 types:- 1) 1-2 cm basalt clasts in off-white clay-rich matrix. 2) Pale green, granular, fine-medium grain size. (c) Limestone - 5-10 cm angular fragments. 2 cm Mn coating.	30	Sulphur yellow, soft + friable. Mottled with rust-coloured areas. Heavy oxide penetration.
O64	4/7				15	Very pale yellow, friable. Some brown staining. Fawn sediment in a crack.
O64	5/7				15	Mixture of sulphur yellow, friable material and fawn coloured pebble. Heavy oxide penetration.
O64	7/7				15	Light rust brown fine grained breccia; rusty patches. < 0.3 mm oxide granules. Fissures lined with white material.

Appendix 2 Sediment Classification

Sample No.	Position (S,W)	Depth(m)	Sediment Classification	Primary Constituents
			TOKELAU	
K1-2T	1°59' 168°08'	4820	RSO ¹ , siliceous fossil bearing calcareous mud	Calcite, clay minerals, quartz(Q) + feldspar(F), siliceous microfossils, RSO, fish debris, glass, zeolite, aggregates, discoasters.
K1-2B	"	-	Glass, RSO, siliceous fossil rich mud.	Clay minerals, Q and F, siliceous fossils, glass, opaques, RSO, fish debris, palagonite.
K1-4T	6°00' 169°32'	5480	RSO, glass bearing siliceous fossil rich mud	Clay minerals, Q+F, siliceous fossils, glass, RSO, opaques, mica(?), pyroxene, fish debris, palagonite, altered volcanics.
K1-4B	"	"	Glass, RSO bearing siliceous fossil rich mud	Clay minerals, Q+F, aggregates, RSO, spicules, fish debris, zeolites, pyroxene, calcite, pala- gonite, glass.
K1-5T	4°45' 170°13'	5510	Glass bearing siliceous fossil rich mud	Clay minerals, Q+F, siliceous fossils, glass, RSO, calcite, fish debris, pyroxene, palagonite, authi- genic feldspar(?).
K1-5B	"	"	Glass, RSO bearing mud	Clay minerals, Q+F, siliceous fossils, zeolite, fish debris, calcite, aggregates, palagonite, altered volcanics.
K1-6T	4°05' 170°08'	5240	Glass, siliceous fossil bearing, calcite rich mud	Clay minerals, Q+F, calcite, siliceous fossils, glass, palagonite, zeolite, RSO, fish debris, discoasters.
K1-6B	"	"	RSO, glass, siliceous fossil bearing mud.	Clay minerals, Q+F, siliceous fossils, glass, zeolite, altered volcanics, aggregates, composite grains, palagonite, RSO, opaques.
K1-FFG20	6°20' 171°09'	5640	Glass, RSO, siliceous fossil bearing mud.	Clay minerals, Q+F, siliceous fossils, aggregates, glass, RSO, mica, fish debris.
S68-2	3°48' 168°16'	5569	Glass, RSO, siliceous fossil bearing mud	Clay minerals, Q+F, siliceous fossils, RSO, altered volcanics, pyroxene, glass, zeolite, fish debris, aggregates.
M70-32	9°12' 173°59'	4457	Glass, calcite bearing, RSO rich mud	Clay minerals, Q+F, RSO, calcite, zeolite, glass, pyroxene, mica, altered volcanics.
M70-33	6°16' 171°31'	5569	Glass, RSO rich mud	Clay minerals, Q+F, glass, RSO, aggregates, pyroxene, composite grains, altered volcanics, palagonite, zeolite, spicules.
M70-34	3°50' 169°04'	5027	Siliceous ooze	Siliceous fossils, clay minerals, other mineral grains, RSO.
M70-35	0°34' 167°36'	5353	Glass bearing, siliceous fossil, calcite rich mud	Clay minerals, Q+F, calcite, siliceous fossils, aggre- gates, RSO, altered volcanics (?), palagonite (?).
M70-36	1°34' 167°42'	5675	Glass, RSO bearing, siliceous fossil rich mud	Clay minerals, Q+F, siliceous fossils, RSO, calcite, altered volcanics, pyroxene, mica, barite, zeolite, glass, fish debris, aggregates.
M70-38	2°18' 170°59'	5496	Glass bearing, siliceous mud	Siliceous fossils, clay minerals, Q+F, altered vol- canics, mica, calcite, RSO, aggregates, fish debris.
KK72-34	5°37' 167°29'	5134	Glass, siliceous fossil bear- ing mud	Clay minerals, Q+F, siliceous fossils, RSO, volcanic debris, pyroxene, zeolite, fish debris, aggregates, palagonite, goethite.

¹ RSO are taken here to include dispersed Fe-Mn oxides,
micronodules and coated grains.

Appendix 2 (Cont.)

Sample No.	Position	Depth(m)	Sediment Classification	Primary Constituents
CATO 10	7°31' 168°49'	5288	Siliceous fossil, RSO bearing glass rich mud.	Clay minerals, Q+F, altered volcanics, RSO, siliceous fossils, pyroxene, calcite, glass, aggregates, zeolite, fish debris, chlorite(?).
CATO 28	7°24' 168°33'	5471	RSO bearing glass rich mud	Clay minerals, Q+F, altered volcanics, pyroxene, mica, zeolite, spicules, fish debris.
CATO 32	7°12' 168°28'	5182	RSO, siliceous fossil bearing, calcite rich mud	Clay minerals, Q+F, calcite, siliceous fossils, RSO, altered volcanics, pyroxene, discoasters, zeolite, glass, fish debris, aggregates.
SOTWX 1A	7°16' 168°29'	5668	Glass, RSO bearing siliceous fossil rich mud	Clay minerals, Q+F, Siliceous fossils, RSO, glass, zeolite, aggregates, opaques, fish debris, palagonite.
SOTWX 2D	7°12' 168°26'	5507	Glass bearing, siliceous fossil rich mud	Clay minerals, Q+F, glass, pyroxene, siliceous fossils, opaques, zeolite, fish debris, aggregates, RSO, palagonite.
SOTWX 3A	8°31' 168°43'	5145	Glass, calcite, siliceous fossil bearing mud	Clay minerals, Q+F, siliceous fossils, calcite, glass, RSO, pyroxene, aggregates, fish debris, nannofossils, rutile.
SOTWX 4B	8°17' 168°31'	4751	RSO, siliceous fossil bearing calcareous ooze	Calcite, clay minerals, Q+F, siliceous fossils, RSO, aggregates, glass, pyroxene, fish debris.
SOTWX 4C	8°17' 168°31'	4565	RSO bearing calcareous ooze	Calcite, RSO, glass, siliceous fossils, zeolite, clay minerals.
SOTWX 5A	7°29' 168°29'	5619	RSO, glass, siliceous fossils bearing mud	Clay minerals, Q+F, siliceous fossils, glass, RSO, pyroxene, palagonite, zeolite, calcite, aggregates.
STYX4-7	9°37' 170°37'	4162	Calcareous ooze	Calcite, clay minerals, detrital minerals, RSO, spicules, glass
STYX4-10	8°45' 168°55'	5021	Siliceous fossil, RSO bearing calcite rich mud	Clay minerals, Q+F, calcite, RSO, siliceous fossils, zeolite, glass, altered volcanics, pyroxene, fish debris, aggregates, barite.
STYX4-12	7°41' 170°31'	5440	Siliceous fossil, RSO, glass bearing mud	Clay minerals, Q+F, RSO, siliceous fossils, pyroxene, composite grains, altered volcanics, glass, zeolite, aggregates.
STYX 43	4°14' 168°17'	5451	Glass, RSO, siliceous fossil bearing mud	Clay minerals, Q+F, siliceous fossils, aggregates, RSO, zeolite, fish debris, palagonite, altered volcanics, glass
RC12-87	2°18' 163°58'	5243	RSO bearing glassy mud	Glass, clay minerals, Q+F, RSO, zeolite, palagonite, altered volcanics, fish debris, aggregates, opaques.
<u>PENRRHYN BASIN</u>				
RC13-46	5°55' 167°6'	5354	Fish debris, glass, zeolite, RSO bearing mud	Clay minerals, Q+F, RSO, zeolite, glass, fish debris, pyroxene, palagonite, aggregates, opaques.
K2-1	10°16' 157°21'	5510	Glass, RSO bearing zeolitic mud	Clay minerals, Q+F, zeolite, RSO, altered volcanics, pyroxene, fish debris, spicules, glass, aggregates.
C1-1	14°09' 151°40'	4750	Glass bearing, mineral grain, calcite, RSO rich mud	Clay minerals, Q+F, calcite, RSO, glass, spicules, altered volcanics, pyroxene, micromodules, fish debris, zeolite, aggregates, opaques.
C1-3	11°11' 154°31'	5580	Glass, RSO bearing zeolite rich mud	Clay minerals, Q+F, zeolite, RSO, glass, siliceous fossils, altered glass, aggregates.
C1-4	10°39' 155°21'	5560	RSO, glass bearing, zeolite rich mud	Clay minerals, Q+F, zeolite, glass, RSO, spicules, altered volcanics, palagonite, aggregates, fish debris.
C1-7	8°07' 157°22'	5510	RSO, glass, zeolite rich mud	Clay minerals, Q+F, zeolite, spicules, siliceous fossils, RSO, pyroxene, glass, altered volcanics, calcite, fish debris, isotropic grains, aggregates, fish debris.

Appendix 2 Sediment Classification

Sample No.	Position	Depth(m)	Sediment Classification	Primary Constituents
C1-9	7°23' 155°23'	4970	Fish debris, RSO, glass, calcite bearing zeolite rich mud	Clay minerals, Q+F, zeolite, calcite, glass, RSO, spicules, radiolaria, anisotropic mineral grains, aggregates, fish debris.
C1-10	7°18' 156°20'	5170	Glass, RSO, siliceous fossil, fish debris bearing zeolite rich mud	Clay minerals, Q+F, zeolite, siliceous fossils, RSO, anisotropic minerals, glass, altered volcanics, palagonite (?), mica, fish debris, aggregates.
C1-13	6°11' 159°09'	5390	Fish debris, siliceous fossil bearing zeolite rich mud	Clay minerals, Q+F, zeolite, siliceous fossils, RSO, aggregates, anisotropic grains, glass, altered volcanics(?), aggregates, fish debris.
C1-15	7°55' 158°11'	5520	Fish debris, RSO bearing zeolite rich mud	Clay minerals, Q+F, zeolite, RSO, glass, altered volcanics, siliceous fossils, calcite, fish debris, aggregates
C1-16	8°54' 158°56'	5650	Fish debris, zeolite bearing mud	Clay minerals, Q-F, zeolite, RSO, siliceous fossils, altered volcanics, mica, pyroxene, calcite, aggregates, fish debris
C2-1	10°12' 159°31'	5300	RSO bearing zeolite rich mud	Clay minerals, Q+F, zeolite, RSO, spicules and spines, calcite, aggregates, glass, altered volcanics, fish debris.
M70-17	7°32' 161°35'	4721	Zeolite, RSO bearing glass rich mud	Clay minerals, Q+F, RSO, zeolite, spicules, aggregates, glass, pyroxene, opaques, calcite.
STYX 35	4°17' 160°57'	5262	Glass bearing siliceous mud	Clay minerals, Q+F, siliceous fossils, aggregates, RSO, zeolite, calcite, fish debris, glass.
STYX 58	3°54' 155°47'	5065	Calcite bearing siliceous fossil rich mud	Clay minerals, Q+F, siliceous fossils, calcite, RSO, glass, zeolite, fish debris, pyroxene, aggregates, opaques.
STYX 66	3°54' 155°47'	5187	Glass, RSO bearing siliceous fossil, calcite rich mud	Clay minerals, Q+F, calcite, siliceous fossils, RSO, zeolite, aggregates, glass
KK72-32	7°39' 161°35'	4569	RSO, spicule bearing calcite rich mud	Clay minerals, Q+F, calcite, spicules, radiolaria, RSO, zeolite, palagonite, fish debris, discoasters, glass
KK72-33	7°27' 162°12'	4613	Siliceous fossil bearing, calcareous ooze	Nannofossils, foram fragments, siliceous fossils, clay minerals, Q+F, RSO, discoasters, altered volcanics, glass, aggregates
RC13-66	4°49' 152°38'	5332	RSO, siliceous fossil bearing mud	Clay minerals, Q+F, siliceous fossils, RSO, zeolite, glass, opaques, aggregates, fish debris
V18-267	12°17' 161°03'	2760	Glass, calcite rich mud	Glass, calcite, zeolite, Q+F, clay minerals, RSO, opaques, altered volcanics, pyroxene, palagonite, discoasters
V18-275	12°44' 160°56'	3623	RSO, calcite bearing glassy mud	Clay minerals, Q+F, glass, calcite, RSO, zeolite, aggregates
V18-276	12°42' 160°49'	3587	Zeolite bearing glassy mud	Glass, clay minerals, Q+F, zeolite, opaques, pyroxene, calcite, fish debris, palagonite
V18-277	12°42' 160°45'	3952	Vitric ash	Glass, Q+F, clay minerals, zeolite, opaques, fish debris, palagonite, RSO
V18-278	12°42' 160°39'	4738	Fish debris bearing zeolitic ash	Glass, zeolite, fish debris, clay minerals, Q+F, RSO, opaques
V18-279	12°42' 160°37'	4753	Glass bearing calcareous mud	Calcite, glass, clay minerals, Q+F, zeolite, palagonite, RSO, opaques, aggregates, fish debris, discoasters
V18-280	12°27' 159°23'	4989	Zeolite, RSO, glass bearing mud	Glass, clay minerals, Q+F, RSO, zeolite, calcite, pyroxene, palagonite, opaques, aggregates, fish debris
V18-281	12°26' 158°20'	5393	RSO, zeolite rich mud	Clay minerals, Q+F, zeolite, RSO, fish debris, aggregates, opaques, palagonite, calcite

Appendix 2 (Cont.)

Sample No.	Position	Depth(m)	Sediment Classification	Primary Constituents
V18 283	12°51'	4936	RSO, calcite bearing zeolite rich mud	Clay minerals, Q+F, zeolite, calcite, RSO, spicules, fish debris, aggregates, opaques
V18-284	14°05' 155°08'	4967	Zeolite bearing mud	Clay minerals, Q+F, zeolite, glass, pyroxene, fish debris, glass, RSO, aggregates, opaques
<u>EAST LINE ISLANDS</u>				
K2-5	9°13' 151°53'	4870	Fish debris bearing calcite rich zeolitic mud	Clay minerals, Q+F, zeolite, calcite, fish debris, RSO, siliceous fossils, pyroxene, altered volcanics, aggregates
K2-10	11°38' 148°57'	5170	Zeolitic mud	Clay minerals, Q+F, zeolite, siliceous fossils, calcite, RSO, pyroxene, altered volcanics, aggregates, fish debris, glass
K2-11	12°08' 148°59'	4900	Fish debris, RSO bearing zeolitic mud	Zeolite, clay minerals, Q+F, RSO, pyroxene, altered volcanics, fish debris, spicules, glass, calcite, aggregates
K2-13	12°38' 149°00'	4870	Glass, fish debris, RSO, calcite bearing zeolite rich mud	Clay minerals, Q+F, zeolite, calcite, RSO, altered volcanics, composite grains, pyroxene, siliceous fossils, fish debris, aggregates
K2-14	13°08' 149°07'	4750	Glass, fish debris, RSO bearing zeolite rich calcareous mud	Clay minerals, Q+F, nannofossils, foram fragments, zeolite, RSO, pyroxene, isotropic grains, glass, fish debris, spicules, aggregates
AMPH 116	11°26' 149°17'	5106	Fish debris, glass, RSO bearing zeolitic mud	Clay minerals, Q+F, zeolite, RSO, glass, fish debris, aggregates
AMPH 117	12°24' 148°24'	5151	Fish debris, calcite, glass, RSO bearing zeolitic mud	Clay minerals, Q+F, zeolite, RSO, glass, calcite, fish debris, pyroxene, aggregates, orange globules.
AMPH 126	11°59' 144°22'	4925	Fish debris, calcite bearing zeolitic mud	Clay minerals, Q+F, zeolite, calcite, fish debris, RSO, discoasters.
RC13-70	9°42' 151°24'	4803	Fish debris bearing, calcite, zeolite rich mud	Clay minerals, Q+F, zeolite, calcite, fish debris, RSO, opaques, aggregates, glass
RC13-72	11°36' 150°56'	4980	RSO bearing zeolite rich mud	Clay minerals, Q+F, zeolite, RSO, calcite, micronodules, glass, fish debris, opaques, aggregates, pyroxene, spicules
RC13-73	12°38' 150°46'	4784	Fish debris, RSO, calcite bearing zeolitic mud	Clay minerals, Q+F, zeolite, calcite, RSO, fish debris, glass, pyroxene, opaques, aggregates, heavies, authigenic feldspar
K3-1	6°58' 149°42'	5230	RSO, zeolite, siliceous fossil bearing mud	Clay minerals, Q+F, siliceous fossils, zeolite, RSO, pyroxene, aggregates, mica, fish debris, glass
K3-2	5°47' 150°13'	5390	Glass, RSO, siliceous fossil bearing mud	Clay minerals, Q+F, siliceous fossils, RSO, glass, zeolite, aggregates, glass, calcite, fish debris
K3-3	3°57' 150°59'	4750	Siliceous fossil bearing calcareous age	Calcite, siliceous fossils, clay minerals, Q+F, RSO, glass, zeolites, aggregates
K3-4	2°28' 151°57'	4690	Calcareous ooze	Calcite, clay minerals, siliceous fossils, Q+F, RSO aggregates, glass
K3-5	0°01'N 153°29'	4760	Siliceous fossil bearing calcareous ooze	Foraminifera, nannofossils, siliceous fossils, RSO, clay minerals, Q+F, mineral grains, aggregates

Appendix 3

Chemical Analytical Techniques

(i) Bulk chemical attack

250 mg of dried, finely ground sample were accurately weighed and placed into clean P.T.F.E. beakers. For ferromanganese oxide samples, their hygroscopic nature required that samples were first dried over silica gel for 48 hours prior to weighing. For these same samples, 2 cm³ of 6M HCl were added and the beakers warmed to break down the Mn oxides prior to the addition of the main reagents - 3 cm³ concentrated nitric acid, 3 cm³ concentrated perchloric acid and 10 cm³ 40% hydrofluoric acid. The beakers were heated on a hotplate until dense, white fumes were seen, at which point a further 2 cm³ of hydrofluoric acid were added. The beakers were then gently evaporated to dryness overnight and a further 2 cm³ perchloric acid added.

When fuming ceased, 5 cm³ 6M HCl were added to each beaker to dissolve the residual pellet. For samples rich in Mn, a few drops of hydrogen peroxide were added to aid this process. The remaining solutions were made up to 25 cm³ in volumetric flasks, yielding a final solution matrix close to 1M HCl.

All samples were analysed, often in duplicate, for a standard 10 element suite (Mn, Fe, Cu, Ni, Co, Pb, Zn, Ca, Al, Ti) using a Perkin Elmer 5000 atomic absorption spectrophotometer with a deuterium background correction facility. For quality control purposes, each analytical sample batch contained 5% reagent blanks, 5% internal and/or external reference materials and 10% duplicated samples. The accuracy of the bulk attack, based on the replicate analysis of four nodule standards analysed at six independent German laboratories, is given in Table A. The precision of the analysis based on the duplicate samples is also given in Table A.

Following the same procedures, the LI crusts were also analysed by inductively coupled plasma source spectrometry in order to obtain data for a further 12 elements -

Li, Be, Cr, K, Mg, P, Sr, Ba, Mo, V, Ag and Cd. Whilst the precision of these analyses is generally excellent (Table B), a comparison of the ICP data with the 10 element AAS data indicates that several elements are depressed on the ICP (Table B), both with respect to external standards (determinations by AAS) and values determined on the same samples by AAS.

Of the two main forms of interference, i.e. translational and rotational, it is the latter, due to variations in nebuliser performance and changes in the excitation conditions in the plasma caused by the matrix elements, which cause a depression in instrument sensitivity (Thompson et al. 1982). Whilst occurring in both AAS and ICPS, it appears that for the present sample type rotational interference is enhanced in the latter. At present, the chemical complexity of the solution matrix for Fe-Mn nodules and crusts precludes the possibility of corrections being made to counteract the interference effects.

(ii) Acidified hydroxylamine hydrochloride attack

Half a gram of material (1g in the case of high-carbonate samples) was accurately weighed into a conical 50 cm³ flask fitted with a ground glass stopper. To this 25 cm³ of a mixture of 3 vols. 35% (v/v) acetic acid plus 7 vols. 25% (w/w) hydroxylamine hydrochloride were carefully added. The flasks were shaken for 60 seconds and left overnight.

The contents were filtered and washed with deionised water through a pre-weighed 0.45 µm membrane filter and the filtrate transferred to a 100 cm³ beaker. These were covered with watch glasses and transferred to a hot plate. When the contents had evaporated to about 10 cm³, 2 cm³ of concentrated nitric acid were added drop by drop to destroy the excess reagent. Evaporation was continued until fumes of nitric acid were evolved. The beaker was cooled and the contents transferred to a 25 cm³ volumetric flask and made up to the mark with 1M HCl. The filter paper and residue were dried in a dessicator and weighed,

from which the weight percentage of each sample soluble in the acid reducing agent was calculated.

Analysis was by AAS as for the bulk chemical attack. In the absence of similarly leached external standards, no determination of accuracy was possible. Measurements of precision were made using duplicated samples; the results are shown in Table C.

(iii) Ammonium oxalate-oxalic acid

Half a gram of sample was accurately weighed into a 50 cm³ conical flask fitted with a ground glass stopper. To this 25 cm³ of a pH3 mixture of 0.2M oxalic acid and 0.2M ammonium oxalate were added, shaken for 60 seconds and left to stand in the dark for 2 hours. Exactly as in the acid reducing attack, the solution was filtered and the filtrate placed into a 100 cm³ beaker. To this 2 cm³ of 30% hydrogen peroxide were added to destroy the oxalic acid. The contents were evaporated to approximately 5 cm³ and the cooled solution transferred to a 25 cm³ volumetric flask and made up to 25 cm³ with 1M HCl. As for as the acid reducing attack, the weight of residue and leached material were determined.

Analysis was by AAS as for the bulk chemical attack. Tests were not made to consider interference effects from the extractant. Firstly, it was considered that the peroxide would effectively destroy the oxalic acid and oxalate; secondly, Peachey and Breward (1980) found that the presence of oxalate in the solution matrix introduced less than 5% error in the determination of each element at an analyte level of 1 µg/ml.

Levels of precision were better than 5% for Mn, Fe, Cu, Ni, Co, Al and Ti, but only 30% for Zn, 50% for Pb (analyte near detection limit) and 70% for Ca (Table C).

(iv) Analysis for rare earth elements

19 crust samples, plus 3 duplicates, 3 reference materials and 5 blanks were analysed for La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Lu by inductively coupled plasma source spectrometry at King's College. Samples were selected to represent the whole suite of LI material. Crusts with high Mn/Fe ratios, Mn/Fe ratios approaching unity, with high Al and with high Ca contents were all represented. In addition 3 samples from crust 062 1/3 were analysed, given its unique transition element geochemistry.

Sample preparation was as follows:- 0.500 g of sample powder (200 mesh) was weighed into a clean P.T.F.E. beaker. 4 cm³ of 'A.R.' perchloric acid plus 15 cm³ of A.R. hydrofluoric acid were added and the contents evaporated to dryness. 5 cm³ of concentrated HCl followed by 5 cm³ of deionised water were added, warmed, and a further 5 cm³ of acid and water added until the salts were completely dissolved. The solutions were filtered through a No. 42 ashless filter paper into a glass beaker. The filter paper was ignited in a platinum dish, starting at room temperature and raising the temperature to 900°C. On cooling, 0.500 g of LiBO₂ were added and the mixture fused at 1000°C for 45 minutes. The fusion cake was then dissolved by adding 2.5 cm³ of concentrated acid, warming, and adding 10 cm³ of water. This solution was added to the glass beaker and the process repeated. The solution in the beaker was made to 200 cm³ with water, and an aliquot of 100 cm³ taken.

The REE were then isolated on an exchange column consisting of Bio-Rad AG-50W-X8 resin (H⁺ form, 200-400 mesh). The acidity of the resin was first adjusted to 1.0 N HCl and the sample solution introduced to the column. Unwanted elements were eluted by passing 500 cm³ of 1.75 N HCl through the column. The REE were then eluted with 500 cm³ of 4.0 N HCl, collecting eluted resin on a rapid filter paper.

The resulting solution was evaporated to about 20 cm³, transferred to a 50 cm³ glass beaker and 10 cm³ concentrated nitric acid added. This was evaporated to dryness, and the resulting salts stored. Immediately prior to analysis, the salts were dissolved in 5.0 cm³ of 2N HNO₃.

Precisions were 1% or better for all 12 elements. The level of accuracy, determined on two King's College standards and one Imperial College standard, varied from 9.4% for Lu to 3.0% for Sm, with most elements better than 6% (Table D). Blanks contained approximately 2 ppm La and Ce, 0.1 ppm Nd, Sm + Er, 0.01 ppm Eu, Dy, Yb + Lu and were below detection limits for Pr and Gd.

(v) Lithium metaborate fusion

0.250 g $\pm$ 0.001 g sample, dried over silica gel for 36 hours, were weighed into a clean porcelain crucible. 0.75 g of lithium metaborate (LiBO₂) were mixed intimately with the sample, and the mixture transferred to a graphite crucible. Fusion was carried out in an electric muffle furnace at 1000°C for 30 minutes. The resulting molten bead was poured into a 250 cm³ plastic beaker containing 35 cm³ of 2N HNO₃ and 150 cm³ of water.

The shattered bead was dissolved at room temperature using a magnetic stirrer, and the solution filtered through a number 541 filter paper. The solution was diluted to 250 cm³, and stored in a plastic bottle. Analysis was by inductively coupled plasma spectrophotometry.

By comparison with reference materials, the accuracy of the determinations was better than 3% for SiO₂, Al₂O₃, Fe₂O₃, MgO, K₂O, 4% for CaO, TiO₂, P₂O₅ and MnO, and 7% for NaO. Precisions were better than 3% for all oxides except Na and K, which were better than 5%.

Table A Precision and accuracy of bulk chemical attack based on analysis of external standards and duplicates

Standard	No of determinations	Result	% Mn	% Fe	← Cu	Ni	ppm Co	Pb	Zn	→ % Ca	% Al	ppm Ti
1	5	Reported	29.5	5.2	14800	14600	1600	350	1570	1.78	3.18	0.38
		Found	28.3	4.67	14700	13900	1800	325	1360	1.70	2.62	0.37
		Accuracy	+1.4	+0.66	+300	+900	+70	+40	+50	+0.06	+0.18	+0.02
2	6	Reported	22.3	13.2	5100	7600	2900	750	820	1.93	2.81	0.93
		Found	21.3	12.4	5000	7000	3000	740	700	1.80	2.37	0.95
		Accuracy	+1.7	+0.9	+100	+800	+35	+35	+20	+0.06	+0.19	+0.03
3	3	Reported	19.1	6.7	8000	9500	1700	490	1010	1.45	4.98	0.50
		Found	21.2	6.47	8000	10300	1900	505	920	1.43	4.40	0.54
		Accuracy	+1.1	+0.30	+700	+900	+50	+50	+125	+0.05	+0.09	+0.03
4	3	Reported	31.8	4.26	15200	15200	1700	330	1530	1.66	2.81	0.30
		Found	32.4	4.52	16100	16500	2000	325	1650	1.60	2.33	0.34
		Accuracy	+0.8	+0.20	+900	+500	+50	+20	+125	+0.0	+0.19	+0.03
	% precision	Sediments	5	3	2	5	3	16	2	2	2	3
		nodules	2	3	2	3	1	2	3	2	4	4

Table B Quality control for samples analysed by inductively coupled plasma source spectrometry.
The upper run represents the mean difference between 8 determinations made by ICP of
nodule standards and the reported values obtained by analysis by 6 independent German
laboratories. The difference between the mean AAS value and the mean ICP value is based
on 31 samples

	Mn	Fe	Cu	Ni	Co	Pb	Zn	Ca	Al	Ti
ICP vs. standards mean % difference	0	-14	-5	-12	-12	+7	-7	-10	-19	-17
ICP vs. AAS mean % difference	-5	-16	+1	-16	-21	-1	-9	-12	-11	-25
ICP precision (%)	1	1	1	1	1	1	1	1	1	1
	Li	K	Be	Mg	Sr	Ba	V	Cr	Mo	Ag
	2	1	1	1	1	2	1	5	2	5
	Cd	P								
	3	2								

Table C Determinations of mean precision of acid-reducing attack and ammonium oxalate-oxalic acid attack, using duplicated samples

Attack	No. of duplicates	% Precision									
		Mn	Fe	Cu	Ni	Co	Pb	Zn	Ca	Al	Ti
Acid-reducing	5	5	4	2	3	13	-	36	5	3	19
AO-OA	3	3	2	1	4	2	49	27	69	2	9

Table D Comparison of found and reported REE contents of King's College and Imperial College reference materials. Accuracy based on the more certain Kings' College values

Element		ppm											
		La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu
Material													
KC10	Reported	4.3	9.2	1.6	6.8	1.7	0.75	1.9	2.0	0.43	1.25	1.1	0.16
	Found	4.4	8.0	0.80	6.2	1.6	0.74	1.80	1.96	0.40	1.12	1.02	0.14
KC11	Reported	23	49	5.9	26.5	5.2	1.40	5.0	4.45	1.0	2.7	2.2	0.32
	Found	24.4	49.6	5.40	27.2	5.2	1.28	4.80	4.60	0.90	2.72	2.18	0.30
GA	Reported	38	70		25?	5?						2?	
	Found	40.6	77.4	7.4	30.8	5.0	1.08	4.00	3.54	0.70	2.20	1.98	0.30
%	Accuracy	4	7	9	6	3	5	5	3	9	6	4	9

APPENDIX 4
DATA

Table E Bulk chemical composition of the Line Islands
crusts. Mn, Fe, Ca and Al are in weight %.
Other elements in ppm.

<u>Sample</u>	<u>Position</u>	<u>Depth (m)</u>	<u>Crust thickness (mm)</u>
041 1/1	2°05' N 157°21' W	1350-1550	5
044 2/2	7°35' S 151°33' W	1880-2100	5
045 6/13A	9°04' S 150°42' W	1300-1450	20-25
045 6/13B	"	"	"
050 4/6A	11°03' S 150°06' W	4250-4400	30
050 4/6B	"	"	"
051 2/7	12°53' S 150°46' W	3000-3200	2
051 3/7A	"	"	12
051 3/7B	"	"	"
051 5/7A	"	"	30
051 5/7B	"	"	"
051 5/7C	"	"	"
051 6/7A	"	"	15
052 4/7	15°01' S 149°02' W	3400	1
053 1/1A	13°02' S 147°56' W	4700	6
053 1/1B	"	"	"
053 1/1C	"	"	"
053 1/1D	"	"	"
054 1/1	3°38' N 159°31' W	2800	"
055 3/3	4°22' N 159°05' W	2150-2650	2
058 1/2	10°49' N 165°33' W	1150-1325	10
058 2/2A	"	"	30
058 2/2B	"	"	"
059 7/7	12°31' N 167°03' W	3000-3750	5
060 2/4A	13°28' N 165°25' W	3850	20
060 2/4B	"	"	10
060 3/4	"	"	8
060 4/4	"	"	13
061 2/5A	14°59' N 166°06' W	2800	20
061 2/5B	14°59' N 166°06' W	"	15
061 4/5A	"	"	25
061 4/5B1	"	"	35
061 4/5B2	"	"	"
061 4/5B3	"	"	"
062 1/3A	15°09' N 168°06' W	2700	70
062 1/3B	"	"	"
062 1/3C	"	"	"
062 1/3D	"	"	"
062 1/3E	"	"	"
062 1/3F	"	"	"
062 3/3A	"	"	65x60
062 3/3E	"	"	"
062 3/3F	"	"	"
063 1/9	16°26' N 168°09' W	2325	10
063 2/9A	"	"	25
063 2/9B	"	"	"
063 2/9C	"	"	"
063 5/9A	"	"	2
063 5/9B	"	"	1
063 6/9A	"	"	20
063 6/9B	"	"	5
063 8/9	"	"	20
064 2/8	16°26' N 168°09' W	2400	30
064 4/7A	"	"	15
064 4/7B	"	"	"
064 5/7A	"	"	12
064 5/7B	"	"	15
064 7/7A	"	"	15
064 7/7B	"	"	"

Table E (cont.)

Mn, Fe, Ca, Al in
weight %. Other
elements in ppm.

	Mn	Fe	Ca	Al	Li	Se	Cr	Na	K	Mg	P	Ti
041 1/1	29.30	14.36	2.64	.52	1.21	3.6	51.9	16930	3290	11800	3550	10600
044 2/2	26.10	18.30	2.68	.33	.46	3.9	28.4	16010	3130	10480	3400	11800
045 6/13A	27.60	13.74	2.44	.46	.67	4.0	31.0	15460	4020	11230	2890	13800
045 6/13B	28.50	12.30	2.66	.32	4.58	3.7	30.5	15880	3980	11700	2770	13500
050 4/6A	25.00	19.80	2.62	.76	1.25	5.3	29.5	15900	3230	10290	2940	12800
050 4/6B	20.60	18.52	2.64	1.92	5.01	5.3	33.2	15750	4820	10100	4170	9100
051 2/7	19.90	17.86	2.27	.78	1.74	4.4	32.0	24100	3320	12430	3460	9300
051 3/7A	17.40	16.11	2.04	2.88	7.99	4.5	48.3	20500	9660	9930	3010	7800
051 3/7B	18.00	17.14	2.19	2.62	11.60	4.7	47.6	18270	7580	10890	3240	8700
051 5/7A	20.50	21.00	2.97	1.81	2.81	4.8	49.4	14930	4490	10370	4210	9070
051 5/7B	20.20	22.00	2.56	1.40	2.06	5.3	65.5	14150	3880	10340	4290	9380
051 5/7C	20.50	22.30	2.62	1.43	1.48	5.0	47.2	14110	3960	9980	3850	9830
051 6/7A	17.60	15.76	2.03	3.00	10.05	4.2	40.5	19670	9620	10750	2770	8000
052 4/7	17.20	17.00	2.18	1.19	3.81	3.7	35.1	18850	3240	14150	3390	10600
053 1/1A	11.70	11.54	2.04	5.02	31.03	2.3	45.0	24330	20980	12620	4780	8690
053 1/1B	5.32	7.65	2.44	5.82	21.62	1.5	48.5	28340	29080	10240	7040	5130
053 1/1C	5.75	5.68	1.96	6.12	19.97	1.3	40.9	30070	34190	9150	5540	4500
053 1/1D	8.39	6.24	2.00	6.70	37.53	1.5	54.6	27650	29560	11120	1960	4610
054 1/1	23.70	15.30	2.65	.70	1.16	3.4	49.2	22940	3420	11970	3070	9700
055 3/3	15.40	16.10	4.53	.87	5.16	3.2	28.8	37220	3870	13150	11790	5130
058 1/2	21.60	21.00	2.29	.62	.72	5.7	29.7	14610	3840	9610	3150	3900
058 2/2A	29.20	13.03	2.56	.38	1.64	3.8	31.6	16010	4010	12570	3300	10100
058 2/2B	27.90	12.30	5.10	.52	3.72	4.1	36.2	14400	4000	12180	10980	7700
059 7/7	20.30	19.50	2.15	.87	2.21	5.3	28.1	15380	3470	9940	3080	14800
060 2/4A	19.70	18.20	2.30	1.41	4.53	5.0	21.8	15340	4500	10820	3250	13800
060 2/4B	20.30	18.21	2.15	.88	1.92	5.5	31.3	16530	3440	10210	3170	12600
060 3/4	19.20	18.63	2.02	.95	2.39	5.7	32.9	17200	3630	10320	3300	13200
060 4/4	23.10	20.70	2.43	.74	1.51	5.8	31.9	15470	3560	9850	3040	13400
061 2/5A	21.90	19.00	2.49	1.13	2.03	6.0	32.8	16210	4320	9760	3020	12000
061 2/5B	21.80	19.30	2.54	1.20	2.40	5.9	33.8	15640	4510	9750	3000	13700
061 4/5A	23.10	19.90	2.41	.96	1.30	5.8	29.4	15160	4070	9730	3270	14000
061 4/5B1	26.30	18.30	2.46	.36	.60	4.8	28.6	14390	3440	10140	5850	12300
061 4/5B2	21.04	14.30	3.29	1.86	7.19	4.8	48.6	15400	7810	11500	3890	14200
061 4/5B3	24.20	18.00	2.94	.80	2.02	6.4	43.4	13520	4260	10110	2670	11200
062 1/3A	20.80	18.46	2.16	.94	1.30	7.1	29.9	13810	4040	9450	2320	13800
062 1/3B	19.90	16.85	2.10	1.95	3.65	9.9	36.7	13740	6680	9190	2380	9700
062 1/3C	20.90	19.50	2.13	1.00	1.69	11.5	58.0	12000	4760	9500	2180	12000
062 1/3D	18.50	20.62	1.88	1.24	4.75	12.8	32.8	11010	5400	9680	1980	14300
062 1/3E	19.30	17.79	1.97	1.27	3.75	11.0	29.7	11820	7260	9090	3040	11000
062 1/3F	18.00	19.62	2.08	1.43	3.72	13.5	33.8	11060	7120	8680	3540	17400
062 3/3A	17.70	16.00	2.86	2.97	5.10	5.2	33.4	17460	10080	9380	3310	13000
062 3/3E	19.60	21.60	2.13	.93	1.59	5.8	29.1	13490	3470	9760	3160	12700
062 3/3F	19.50	15.80	2.40	2.74	4.77	5.1	35.0	18270	10340	9700	3280	13200
063 1/9	21.30	17.36	2.23	1.00	2.83	5.2	41.4	15410	4350	11200	3000	13900
063 2/9A	24.70	16.27	2.26	.62	.79	5.0	27.6	14360	3680	9860	4560	13700
063 2/9B	22.00	15.53	2.85	1.21	2.54	6.0	39.9	15280	5620	9990	2940	14000
063 2/9C	23.20	16.11	2.36	.94	1.60	5.0	34.5	15940	4500	10300	3470	15300
063 5/9A	21.00	21.90	2.25	.86	1.52	5.3	37.2	18260	3940	9920	3260	15200
063 5/9B	15.60	17.60	2.16	1.51	6.36	4.4	37.6	39590	7320	14270	3470	13300
063 6/9A	22.80	18.45	2.20	.57	.99	5.2	28.6	14980	3770	10210	11200	14600
063 6/9B	13.20	16.00	5.03	2.31	7.52	4.0	41.8	16690	5940	10170	3870	13100
063 8/9	20.40	18.45	2.14	.82	2.10	5.2	11.6	16670	3910	10320	3430	13300
064 2/7	21.80	20.80	2.45	1.05	2.21	5.5	35.0	13910	3940	9940	7470	15300
064 4/7A	16.40	15.80	3.50	2.98	12.30	4.4	49.9	16550	7060	12140	4500	15500
064 4/7B	20.30	18.00	2.70	1.98	6.85	5.6	42.2	17390	5240	11350	3340	16600
064 5/7A	20.40	22.70	2.26	.87	1.5	5.5	31.71	14320	3760	9790	3320	14200
064 5/7B	20.60	20.80	2.20	.94	1.8	5.3	36.07	14240	3820	9890	2520	13700
064 7/7A	22.20	18.30	2.32	1.37	3.9	6.2	46.68	16930	5430	10500	2620	14200
064 7/7B	23.10	20.00	2.39	1.19	2.5	6.6	31.55	16120	4470	10090	3580	14900

Table E (cont.)

All elements in ppm.

	Co	Sr	Ba	Cu	Ni	Pb	Zn	Mo	V	Ag	Cd
041 1/1	11600	1310	1063	306	5700	1601	675	660	633	6.5	6.3
044 2/2	9300	1384	1059	428	5400	1372	625	562	611	5.7	5.4
045 6/13A	10500	1319	855	689	6900	1331	763	549	572	5.9	6.9
045 6/13B	11500	1318	891	631	7600	1635	788	605	565	6.8	7.4
050 4/6A	6000	1282	1300	1006	3700	855	461	603	613	6.0	4.0
050 4/6B	4600	1063	1266	1235	3900	703	480	436	511	3.9	3.0
051 2/7	3800	1209	1007	1240	3200	692	540	409	590	4.3	3.5
051 3/7A	3160	966	1233	3090	4000	456	573	317	467	3.5	3.0
051 3/7B	3160	1001	1280	2245	4300	524	653	304	480	3.4	3.7
051 5/7A	3770	1153	1306	1912	4100	479	520	409	517	4.2	3.3
051 5/7B	4060	1241	1314	1942	3800	537	580	454	565	10.0	5.1
051 5/7C	3840	1196	1307	1960	3700	555	570	424	553	4.4	3.1
051 6/7A	3090	948	1262	3306	4200	458	610	302	442	3.2	3.4
052 4/7	4850	1108	516	585	2560	765	496	274	504	4.4	3.2
053 1/1A	2520	500	960	2250	4400	390	497	171	316	3.8	3.6
053 1/1B	890	329	686	1071	2000	161	259	69	170	3.0	1.4
053 1/1C	907	274	607	1292	2500	130	250	100	163	2.9	1.7
053 1/1D	1070	310	628	2460	4500	165	382	146	205	3.0	3.7
054 1/1	8000	1204	962	474	5300	774	590	451	547	5.5	5.5
055 3/3	2320	1545	1785	592	3700	313	513	275	448	2.4	3.1
058 1/2	6600	1323	1402	796	3100	1356	587	482	588	6.2	4.3
058 2/2A	15700	1316	845	591	6900	1661	703	778	618	6.1	8.1
058 2/2B	11200	1368	621	607	7000	1556	718	738	579	5.5	7.0
059 7/7	5470	1217	1322	1209	2800	1234	538	359	584	4.6	3.9
060 2/4A	4830	1125	1235	949	2600	1054	519	374	528	4.6	3.3
060 2/4B	4960	1251	1351	987	2980	1115	545	448	579	5.6	4.2
060 3/4	5200	1222	1401	964	2600	1187	540	369	545	4.9	4.0
060 4/4	5600	1286	1367	1358	3300	1081	570	496	600	5.8	4.0
061 2/5A	5400	1234	1596	2006	3700	930	560	447	543	5.6	3.6
061 2/5B	5500	1253	1746	1641	3500	912	580	427	555	4.5	3.7
061 4/5A	5900	1321	1480	1366	3700	1014	565	511	581	6.0	4.0
061 4/5B1	9400	1327	1382	936	4400	1334	565	596	613	6.5	5.2
061 4/5B2	4950	1143	1501	1690	4900	709	550	404	488	4.6	4.8
061 4/5B3	5130	1388	1880	1750	3800	683	620	473	618	4.7	3.7
062 1/3A	4640	1362	1718	1769	3300	1004	593	439	565	4.7	3.5
062 1/3B	3540	1316	2382	2730	3580	575	637	401	561	3.5	2.5
062 1/3C	2910	1530	3029	3250	3250	1019	780	714	835	5.7	2.0
062 1/3D	2380	1447	1202	3470	3350	1363	698	622	841	4.8	2.9
062 1/3E	2350	1427	1637	3160	3480	1754	767	651	745	4.7	2.6
062 1/3F	2440	1579	1924	2550	2370	2374	630	485	752	5.5	3.1
062 3/3A	4310	1066	2029	3652	3600	705	545	252	388	4.1	3.1
062 3/3E	4940	1279	1373	1132	2500	1269	557	405	579	4.6	3.2
062 3/3F	5300	1068	1722	2470	4200	734	545	313	399	4.4	3.6
063 1/9	7700	1310	1442	1148	4100	1299	577	457	561	5.4	4.3
063 2/9A	7100	1309	1305	1122	4100	1471	565	506	576	5.0	3.8
063 2/9B	5700	1330	1364	1600	4300	1064	625	419	528	4.6	4.3
063 2/9C	7500	1286	1477	1342	4400	1353	594	467	540	5.8	4.6
063 5/9A	6000	1291	1307	746	2900	1406	540	438	563	5.1	3.6
063 5/9B	4440	1012	324	754	2900	1168	565	231	421	3.5	3.3
063 6/9A	8400	1364	1324	547	3300	1493	528	477	584	5.0	3.7
063 6/9B	3290	990	1636	1238	3000	847	558	155	363	4.1	3.5
063 8/9	6300	1313	1313	583	2670	1445	535	444	578	4.8	3.4
064 2/7	5400	1268	1469	1276	3500	1300	560	450	562	5.1	3.5
064 4/7A	2700	1036	2761	2505	3900	782	570	193	343	4.3	3.8
064 4/7B	4560	1147	1601	1860	4000	973	952	333	496	5.0	3.4
064 5/7A	7000	1299	1402	668	2900	1426	565	412	566	5.2	3.5
064 5/7B	7700	1246	1402	784	3000	1438	567	393	537	5.3	3.8
064 7/7A	5400	1323	1565	1868	4200	935	625	467	545	5.5	3.9
064 7/7B	4830	1353	1607	1899	3900	875	600	471	557	6.4	3.8

Table F Bulk compositions of nodules analyses at Imperial College

Sample	Position	Depth (m)	% ←-----→					ppm ←-----→					Identification on sample location map
			Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb	Zn	
C1-3M	11°21' 154°31'	5580	18.60	16.70	1.82	2.88	1.09	2360	4100	4040	990	430	1
C1-3F	"	"	18.50	15.40	1.80	2.80	1.00	2200	3800	3900	880	410	1
C1-4F	10°39' 155°21'	5560	20.60	13.30	1.75	2.70	0.94	3400	6100	4200	810	530	2
C1-4L	"	"	16.10	13.20	1.68	4.04	0.92	1930	4200	3210	640	430	2
C1-5	9°53' 156°17'	5580	15.80	27.80	1.60	3.10	1.80	1200	2000	4200	1450	580	3
C1-6A	9°24' 157°17'	5390	20.60	16.30	1.78	2.10	1.24	2700	4950	4780	1040	560	4
C1-6B	"	"	21.40	16.30	2.02	1.71	1.17	1780	3400	4990	990	430	4
C1-7	8°07' 157°22'	5510	19.50	11.70	1.95	3.60	0.99	2600	5500	3400	730	550	5
C1-8S	7°56' 156°23'	5250	20.70	11.37	1.57	3.44	0.88	4530	8000	2810	610	670	6
C1-8L	"	"	19.90	11.54	1.82	3.65	0.80	3980	6200	3280	690	590	6
C1-10	7°18' 156°20'	5170	30.40	6.40	1.6	3.00	0.36	10700	12100	2000	350	1420	7
C1-13	6°11' 159°09'	5390	27.90	7.00	1.55	2.75	0.36	8300	10700	2200	300	1230	8
C1-15	7°55' 158°11'	5520	25.70	7.55	1.7	3.90	0.50	9300	10900	2200	490	1090	9
C1-16	8°54' 158°56'	5650	16.20	10.00	1.4	4.40	0.69	4800	9900	2000	560	710	10
C2-1F	10°12' 159°31'	5300	18.30	17.20	1.75	2.45	1.21	2600	4100	4500	1080	500	11
C2-1L	"	"	17.00	13.90	1.80	3.90	0.99	1700	3300	3500	770	450	11
K2-1	10°16' 157°21'	5510	25.40	11.75	1.65	4.01	0.89	5890	10100	2840	760	750	12
STYX 36S	4°17' 160°57'	5262	8.24	6.37	1.52	6.46	0.32	2990	3400	1010	150	440	13
STYX 36M	"	5027	15.80	7.02	1.94	5.08	0.47	5100	5600	1810	380	660	13
STYX 37	"	5103	20.10	8.87	1.71	3.91	0.50	5960	7900	2000	400	720	13
AMPH 86G	"	"	19.70	13.90	2.00	3.50	1.10	3560	5960	3330	830	640	16
STYX64FF16	3°54' 155°47'	4939	21.00	9.44	2.00	2.80	0.56	7670	9180	1840	280	1000	31
STYX58 FF7	"	5065	11.87	10.98	1.80	4.40	1.00	3280	4510	1630	390	550	32
STYX56 FF1	"	4904	29.60	7.60	1.70	2.00	0.33	11100	10500	1880	330	1650	32
STYX27 FF1	3°45' 156°03'	5065	11.98	12.18	1.10	4.80	1.11	3540	5460	1410	310	650	33
AMPH 100G	3°40' 156°37'	5115	15.31	9.86	1.60	4.10	0.70	4940	6430	2010	410	590	34
AMPH 92P	5°56' 158°39'	5283	12.41	16.08	1.40	3.50	0.80	1280	1450	1030	870	470	38
AMPH 117P	12°24' 148°24'	5151	21.80	10.23	1.80	3.30	0.80	6180	10400	2470	470	880	40
AMPH 125PG	11°20' 144°35'	?	25.90	8.30	1.80	3.30	0.47	10100	9900	1770	300	1170	41
K3-1A	6°58' 149°42'	5230	33.70	4.64	1.55	2.50	0.26	12100	11500	1300	140	1850	42
K3-1B	"	"	32.90	5.71	1.60	2.45	0.34	10900	11000	1500	200	1700	42
K3-1	"	"	27.50	8.07	2.02	2.54	-	7920	10420	2280	340	1290	42
K3-1 Top	"	"	24.90	8.78	1.68	2.85	-	9220	10000	1720	390	1070	42
K3-3	3°57' 150°59'	4750	15.20	8.60	1.75	4.25	0.44	6500	8000	1300	260	710	43
K3-4	2°28' 151°57'	4690	25.30	12.40	2.05	1.75	0.77	6800	11000	2100	550	930	44
K1-F4	2°59' 168°02'	5460	28.00	6.00	1.75	3.00	0.52	12600	12200	1500	200	1330	45
K1-F6S	2°01' 169°30'	4820	18.30	16.50	1.80	1.90	1.16	3400	4900	2900	780	550	46
K1-F6N	"	"	18.00	17.50	1.80	1.60	1.20	2300	3000	3600	910	480	46

Table F (Cont.)

Sample	Position	Depth (m)	%					ppm					Identification on sample location map
			Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb	Zn	
K1-F6L	2°01' 169°30'	4820	19.70	18.50	1.90	1.60	1.17	2600	4400	3600	880	520	46
K1-F8	4°01' 169°31'	5350	18.70	18.40	1.80	2.00	1.59	2500	4000	3600	910	500	47
K1-F9S	5°00' 169°29'	5310	14.00	19.30	1.85	2.45	2.00	1700	2600	2600	820	520	48
K1-9LA	"	"	15.50	20.60	1.80	1.80	1.77	1500	2400	3300	980	510	48
K1-9LB	"	"	18.90	18.30	1.90	1.90	1.70	1800	3300	4200	970	550	48
K1-F10	6°00' 169°32'	5480	18.30	16.30	1.80	2.80	1.53	2400	4400	2600	790	510	49
K1-F13	3°45' 170°16'	5510	18.90	13.10	2.10	3.30	1.13	6100	660	1900	300	740	50
K1-F17	4°14' 171°05'	5300	15.90	19.10	1.80	2.50	1.41	1900	2800	2900	870	490	51
K1-2	1°59' 168°08'	4820	17.10	11.27	1.53	3.76	1.41	5190	6610	2030	410	850	52
K1-4	6°00' 169°32'	5480	17.60	16.70	1.80	3.10	1.50	2100	4000	3500	780	1390	49
K1-6	4°05' 170°58'	5240	18.30	18.80	1.80	2.00	1.37	2100	3400	3700	940	490	53
RC13-45	8°33' 167°00'	3940	19.20	17.80	2.30	1.80	1.15	1400	3200	3900	790	510	54
RC13-46TW	5°55' 167°06'	5354	9.82	6.72	1.61	5.33	0.60	1040	1490	1820	370	250	55
RC13-70	9°42' 151°24'	4803	18.20	9.63	1.60	2.74	0.64	4610	7480	2480	490	680	56
RC13-72	11°56' 150°56'	4980	20.30	12.30	1.75	2.75	1.00	3600	6000	3300	610	590	57
RC13-73	12°38' 150°46'	4784	18.00	15.40	2.10	2.35	1.31	2000	4200	4100	800	500	57
V18-283	12°51' 156°11'	4936	21.40	14.40	1.55	2.60	1.24	3600	6500	4000	770	590	59
V19-284	14°05' 155°08'	4987	17.90	15.20	1.90	3.20	1.50	2000	4000	3400	710	810	60
CATO-10	7°31' 168°49'	5288	13.92	20.46	2.00	2.00	1.70	770	1050	2530	900	580	67
CATO-28	7°24' 168°33'	5471	13.45	19.06	1.56	1.54	1.36	1110	1270	3070	850	570	68

Table 1. Bulk Composition of S.W. Pacific Sediments

Sample	Position		Depth (m)	Mn	Fe	Ca	Al	Ti	Cu	Ni	Co	Pb	Zn	Identification on sample loc- ation map
	S	W												
K1-2T	1°59'	168°08'	4820	0.39	2.69	17.30	3.30	4200	172	122	51	17	75	52
K1-2B	"	"	"	0.63	5.28	1.60	5.50	7700	229	123	80	35	119	52
K1-4T	6°00'	169°32'	5480	0.51	6.12	2.45	5.90	10800	186	107	71	42	123	49
K1-4B	"	"	"	0.65	7.06	2.25	6.40	11800	285	127	92	39	139	49
K1-5T	4°45'	170°13'	5510	0.55	5.65	1.98	5.70	8500	217	218	74	49	124	136
K1-5B	"	"	"	0.64	6.42	2.10	6.35	9000	234	160	90	42	137	136
K1-6T	4°05'	170°58'	5240	0.44	4.00	8.70	5.10	6000	170	104	61	35	136	53
K1-6B	"	"	"	0.58	5.16	2.00	5.60	8000	253	142	81	45	247	53
S68-PC2	3°48'	168°16'	5569	0.50	5.29	1.95	5.50	7900	183	125	70	50	368	137
M70-32	9°12'	171°59'	4457	1.05	7.45	3.95	6.55	4300	723	240	137	49	493	138
M70-33	6°16'	171°11'	5569	0.68	7.21	2.20	7.30	11300	230	260	110	74	259	139
M70-34	3°50'	169°40'	5027	0.13	0.69	0.90	0.96	600	63	60	20	21	172	140
M70-35	0°35'	167°36'	5353	0.40	2.74	7.50	4.40	2500	206	127	60	30	101	141
M70-36	1°34'	167°42'	5675	0.47	4.97	1.45	5.55	6200	431	140	80	59	211	142
M70-38	2°18'	170°59'	5496	0.26	1.93	1.40	3.00	1800	151	95	55	17	82	143
KK72-34	5°37'	167°29'	5134	0.88	4.84	1.70	5.70	5200	310	217	123	53	136	157
CATO 10	7°31'	168°49'	5288	0.63	6.65	2.75	6.40	10300	317	185	100	69	446	67
CATO 28	7°24'	168°33'	5471	0.67	7.04	3.00	7.15	13000	320	230	105	40	416	68
CATO 32	7°12'	168°28'	5182	0.54	4.76	7.90	5.25	5100	207	100	70	30	335	63
SOTW10-1A	7°16'	168°29'	5668	0.66	6.48	2.40	6.40	9100	225	145	85	34	205	64
SOTW10-2D	7°12'	168°26'	5507	0.76	6.69	2.45	5.95	8500	260	225	125	62	282	63
SOTW10-3A	8°31'	168°43'	5145	0.50	6.62	3.45	6.15	10000	172	145	70	39	183	147
SOTW10-4B	8°17'	168°31'	4751	0.24	2.29	27.00	2.35	3100	82	60	35	12	76	66
SOTW10-4C	"	"	4565	0.22	1.85	28.50	2.10	3000	75	50	30	27	59	66
SOTW10-5A	7°29'	168°29'	5619	0.54	6.26	2.85	6.35	9900	204	130	80	36	273	65
STYX4-7	9°37'	170°37'	4162	0.11	1.04	36.50	0.84	1100	35	200	14	19	49	78
STYX4-10	8°45'	168°55'	5021	0.47	6.33	6.40	6.20	12300	210	130	75	33	234	76
STYX4-12	7°41'	170°51'	5440	0.51	5.95	2.30	5.85	8800	188	100	75	33	230	79
STYX 43	4°14'	168°17'	5451	0.53	5.29	2.05	5.35	6600	190	120	80	39	474	62
RC12-87	2°18'	163°58'	5243	1.26	6.16	1.35	7.20	5200	587	1050	137	18	235	129
RC13-46	5°55'	167°06'	5354	1.32	5.74	2.35	6.80	6800	546	325	172	44	160	55
K2-1	10°16'	157°21'	5510	1.32	5.98	1.95	5.80	4500	408	275	185	70	121	12
K2-3	9°50'	155°00'	5470	1.51	5.82	2.00	6.05	4500	458	375	205	58	140	148
K2-10	11°38'	148°57'	5170	1.49	5.67	2.50	5.70	3800	448	425	210	43	130	149
K2-11	12°08'	148°59'	4900	1.49	4.97	2.65	5.40	2200	372	390	205	52	118	150
K2-13	13°08'	149°07'	4750	1.48	5.80	4.00	6.00	4000	381	370	205	52	125	151
K2-14	13°38'	149°09'	4660	1.47	4.85	12.60	4.40	3200	329	390	215	35	116	152
C1-1	14°59'	151°40'	4750	0.96	8.63	5.35	6.35	18000	291	240	140	24	174	153
C1-3	11°21'	154°35'	5580	1.81	6.52	1.95	5.95	6200	464	380	265	65	143	1
C1-4	10°39'	155°21'	5560	1.61	5.91	2.10	5.85	5000	410	395	225	84	132	2
C1-7	8°07'	157°21'	5510	0.84	5.95	1.90	6.80	6200	360	250	135	56	122	5
C1-9	7°23'	153°23'	4970	1.52	5.08	4.00	5.90	3600	533	455	220	76	135	154
C1-10	7°18'	156°20'	5170	1.28	5.31	2.65	5.75	2500	551	475	185	80	132	7
C1-13	6°11'	159°09'	5390	1.03	5.28	2.55	5.95	2500	500	315	160	68	138	8
C1-15	7°55'	158°11'	5520	1.09	5.92	2.35	6.10	4000	420	295	165	63	140	9
C1-16	8°54'	158°56'	5650	1.13	6.24	2.45	6.25	3600	396	250	165	49	149	10
C2-1	10°12'	159°31'	5300	1.56	6.36	2.10	6.05	6800	389	325	215	98	155	11
M70-P17	7°32'	161°35'	4721	1.68	5.62	3.45	5.70	3000	687	600	255	84	245	27
AMPH 116	11°26'	149°17'	5106	2.45	6.39	3.00	5.55	2200	652	950	255	38	196	86
AMPH 117	12°24'	148°24'	5151	2.06	6.54	2.95	6.00	4400	412	465	255	68	177	40
AMPH 126	11°59'	144°22'	4875	2.60	6.77	4.20	5.33	590	644	543	293	60	178	155
STYX 35	4°20'	161°00'	5262	0.87	3.69	1.15	4.35	3600	285	225	120	50	443	39
STYX 58	3°54'	155°47'	5065	0.84	3.56	2.95	4.35	3200	285	220	120	63	104	32
STYX 66	3°54'	155°47'	5187	0.73	2.90	6.30	3.85	2800	274	235	115	77	95	32
RC13-66	4°49'	152°38'	5332	1.47	5.46	1.95	6.20	4200	677	400	199	53	179	127
RC13-70	9°42'	151°24'	4803	1.79	5.19	6.60	6.20	5400	427	370	218	55	128	56
RC13-72	11°56'	150°56'	4980	2.00	7.43	2.85	6.10	7700	450	340	247	78	160	57
RC13-73	12°38'	150°46'	4784	2.04	7.52	4.20	6.50	7400	478	370	261	78	166	58
KK72-32	7°39'	161°35'	4569	1.65	5.56	9.40	5.15	3600	513	453	237	52	176	168
KK72-33	7°27'	162°12'	4613	0.43	1.64	30.20	1.90	1700	155	100	68	11	50	156
V18-267	12°17'	161°03'	2760	0.04	5.00	5.00	7.95	4500	77	115	17	-	-	158
V18-275	12°44'	160°56'	3623	1.65	6.47	11.45	6.00	1100	543	650	98	25	-	159
V18-276	12°42'	160°49'	3587	1.58	7.30	2.10	6.70	6000	694	850	241	34	-	160
V18-277	12°42'	160°45'	3952	1.73	4.30	18.60	4.25	1400	346	550	251	60	-	161
V18-278	12°42'	160°39'	4738	4.15	10.50	9.40	4.40	1800	1027	1300	226	82	-	162
V18-279	12°42'	160°37'	4753	0.66	2.83	25.50	2.75	4200	174	115	77	33	-	163
V18-280	12°27'	159°23'	4989	1.84	7.79	2.20	6.65	9100	430	270	229	83	-	164
V18-281	12°26'	158°20'	5393	1.84	7.90	2.00	6.25	7900	447	245	265	81	-	165
V18-283	12°51'	156°11p	4936	1.84	7.33	2.65	6.25	6100	399	335	233	78	163	59
V18-284	14°05'	155°08'	4987	1.75	9.22	2.75	6.50	13300	414	295	211	70	-	60
K3-1	6°58'	149°42'	5230	1.70	5.32	2.15	5.30	4600	529	440	213	52	158	42
K3-2	5°47'	150°13'	5390	1.55	5.20	2.15	5.15	3300	449	355	192	45	271	166
K3-3	3°57'	150°59'	4750	0.12	0.60	34.70	0.82	500	55	45	27	*	49	43
K3-4	2°28'	151°57'	4690	0.08	0.39	34.30	0.73	350	50	35	14	*	26	44
K3-5	0°00'	153°29'	4760	0.10	0.51	31.40	0.90	380	87	45	17	*	26	167

* = below detection limit.

Mn, Fe, Ca and Al in weight %

Ti, Cu, Ni, Co, Pb, Zn in ppm

Table II Composition of the hydroxylamine hydrochloride soluble fraction
of S.W. Pacific sediments, expressed as ppm of the bulk sediment

	Mn	Fe	Cu	Ni	Co	Pb	Zn	Al	Ti
K1 2T	3102	3572	108	92	35	22	45	1353	76
K1 2B	5270	9809	112	62	55	34	51	5831	76
K1 4T	3800	9956	106	42	51	29	58	6517	35
K1 4B	569610690		116	62	78	33	98	4176	32
K1 5T	5219	9248	128	60	63	38	53	6749	30
K1 5B	5757	8702	83	66	72	28	42	4294	32
K1 6T	3968	6138	102	57	44	27	109	3379	69
K1 6B	5491	7582	129	92	63	26	380	6494	63
S68 2	4600	9860	110	52	53	24		6120	53
M70 32	7029	7281	121	143	90	39		1791	25
M70 33	5746	6006	57	138	80	30	97	1872	40
M70 34	1141	972	39	54	23	9	145	864	41
M70 35	3616	4896	136	73	43	16	41	3424	45
M70 36	3924	7974	104	49	56	32	108	5130	54
M70 38	2414	2652	79	70	53	23	46	4318	43
KK72 34	6552	7128	121	142	94	32	95	4680	24
CATO 10	510410070		137	68	73	32		4147	64
CATO 28	4692	9768	114	92	66	24		3564	51
CATO 32	3503	7750	97	47	46	24		3658	101
SOTW10 1A	595010900		113	58	57	26	95	4978	47
SOTW10 2D	768613800		165	114	98	38		6944	72
SOTW10 3A	457310290		93	41	38	24	80	5270	68
SOTW10 4B	1523	2815	37	17	17	5	31	873	314
SOTW10 4C	593	1228	15	6	6	3	18	340	280
SOTW10 5A	412510940		117	51	50	24		6090	64
STYX4 7	1185	2455	31	13	11	5	37	680	232
STYX4 10	3458	8060	97	39	42	23	123	4004	93
STYX4 12	427011190		117	44	48	30	133	6048	56
STYX 43	368010320		108	58	68	24		6024	49
RC13 46	13000	4602	123	268	145	43	57	1989	25
K2 1	1324012750		164	208	154	48	39	2346	21
K2 3	1440012440		205	284	178	50	41	2664	59
K2 10	1484012920		263	293	157	43	46	2440	22
K2 11	1478012120		184	275	165	45	49	2140	14
K2 13	1360015850		210	247	166	54	56	2725	51
K2 14	1465011660		183	254	153	33	50	1320	56
C1 1	782414350		145	122	99	33	58	2904	61
C1 3	1953019420		286	267	218	65	48	4732	40
C1 4	1802015740		224	274	193	60	45	3280	26
C1 7	7424	9180	145	152	102	34	39	3360	26
C1 9	1613011375		254	344	173	45	60	3350	29
C1 10	14030	8988	207	3110	137	36	41	3402	14
C1 13	11420	7463	146	223	121	37	44	3026	15
C1 15	1176010520		161	195	118	39	50	3200	20
C1 16	1086011320		162	187	97	21	25	3717	61
C2 1	1680018430		243	258	211	50	70	4475	85
M70 P17	1714010350		386	568	193	23	113	3151	122
AMPH116	22880	9900	431	799	227	44	101	1958	35
AMPH117	2047019490		259	350	240	24	94	2592	62
AMPH126	2211017940		381	471	237	30	69	2310	69
STYX 35	642610550		207	165	80	32		8874	78
STYX 58	8888	8118	187	210	112	22	31	6534	51
STYX 66	7616	6216	171	193	11	28	31	4228	62
KK72 32	1458010330		277	392	158	36	61	2844	101
KK72 33	1695	2788	41	19	18	5	33	1023	213
RC13 66	13740	7125	210	393	129	45	64	3135	50
RC13 70	1686015690		248	366	109	31	31	3131	217
RC13 72	1939019850		248	317	235	101	62	2829	101
RC13 73	1835017360		260	334	231	48	55	2464	108
V18 267	869	1540	20	39	39	11		1364	
V18 275	16040	4444	363	631	86	22		1606	125
V18 276	14310	5655	228	757	183	15		1965	42
V18 277	17600	6675	195	592	228	25		2525	90
V18 280	1724019560		228	232	178	50		3380	118
V18 281	1581019760		224	220	224	49		3325	93
V18 283	1674017140		207	276	200	49		3534	89
V18 284	1633020520		225	234	178	50		3258	153
K3 1	1523010950		237	384	200	46	55	6693	60
K3 2	14450	7980	227	321	170	21	181	4557	36
K3 3	1060	1423	37	23	15	3	31	495	59
K3 4	730	930	34	18	9	3	11	413	48
K3 5	1008	1180	58	23	10	3	14	480	46

TABLE I POSITIONS AND STATION IDENTIFICATION NUMBERS (FIG.84)
OF NODULE ANALYSES USED IN THIS STUDY. ASTERIXES
MARK ANALYSES PERFORMED AT IMPERIAL COLLEGE

Station	Position		Depth (m)	Identification on sample location map
	S	W		
C1-3*	11°21'	154°31'	5580	1
C1-4*	10°39'	155°21'	5560	2
C1-5*	9°53'	156°17'	5580	3
C1-6*	9°24'	157°17'	5390	4
C1-7*	8°07'	157°22'	5510	5
C1-8*	7°56'	156°23'	5250	6
C1-10*	7°18'	156°20'	5170	7
C1-13*	6°11'	159°09'	5390	8
C1-15*	7°55'	158°11'	5520	9
C1-16*	8°54'	158°56'	5650	10
C2-1*	10°12'	159°31'	5300	11
K2-1*	10°16'	157°21'	5510	12
STYX 36*	4°17'	160°57'	5027	13
STYX 37*	"	"	5103	13
VIT 5988	11°03'	156°09'	5000	14
VIT 5988(4)	11°03'	156°11'	5200	15
VIT 5987	11°00'	156°20'	5200	14
AMPH 86	11°25'	157°37'	5302	16
V18 SBT 121	12°24'	157°49'	5123	17
AMPH 85	11°35'	158°31'	5338	18
RAVAKAI FG11	10°38'	158°32'	5286	19
RAVAKAI FG10	12°24'	158°44'	5310	20
RAVAKAI FG9	14°05'	158°59'	5111	21
VIT 6334	11°06'	159°00'	5300	22
RAVAKAI FG8	14°49'	159°06'	5092	23
AMPH 84	11°40'	159°16'	5146	24
VIT37 5423	10°01'	160°01'	4833	25
VIT37 5422	12°05'	160°26'	5618	26
VIT 5112	6°59'	154°05'	5040	27
VIT 5114	2°59'	154°18'	4980	28
AMPH 110	5°49'	154°39'	4768	29
CNEXO B1	4°59'	155°00'	4690	30
CNEXO B2	"	"	4765	30
CNEXO B4	"	"	4840	30
CNEXO B5	"	"	4990	30
STVY64 FF16*	3°54'	155°47'	4939	31
STYX58 FF7*	"	"	5065	32
STYX56*	"	"	4904	32
STYX27*	3°45'	156°03'	5065	33
AMPH 100*	3°40'	156°37'	5115	34
VIT 6335	5°01'	158°10'	3100	35
CNEXO B11	3°31'	158°30'	5175	36
CNEXO B10	"	"	5150	36
CNEXO B12	2°01'	158°31'	5080	37
CNEXO B13	2°02'	158°30'	5100	37
CNEXO B6-B9	3°30'	158°31'	5150	36
AMPH 92*	5°56'	158°39'	5283	38
STYX 36	4°17'	160°57'	5027	39
AMPH 117P	12°24'	148°24'	5151	40
K3-1*	6°58'	149°42'	5230	42
K3-3*	3°57'	150°59'	4750	43
K3-4*	2°28'	151°57'	4690	44
K1-4*	2°59'	168°02'	5460	45
K1-6*	2°01'	169°30'	4820	46

TABLE I (Cont.)

Station	Position		Depth (m)	Identification on sample location map
	S	W		
K1-8*	4°01'	169°31'	5350	47
K1-9*	5°00'	169°29'	5310	48
K1-10*	6°00'	169°32'	5480	49
K1-13	3°45'	170°16'	5510	50
K1-17*	4°14'	171°05'	5300	51
K1-GC2	1°59'	168°08'	4820	52
K1-GC4*	6°00'	169°32'	5480	49
K1-GC6*	4°05'	170°58'	5240	53
RC13-45*	8°33'	167°00'	3940	54
RC13-46*	5°55'	167°06'	5354	55
RC13-70*	9°42'	151°24'	4803	56
RC13-72*	11°56'	150°56'	4980	57
RC13-73*	12°38'	150°46'	4784	58
V18 283*	12°51'	156°11'	4936	59
V18 284*	14°05'	155°08'	4987	60
ERDC2 05	1°16'	168°58'	6965	61
STYX 46	4°14'	168°17'	5204	62
SOTWX 2FFD	7°12'	168°26'	5507	63
CATO 32P	7°12'	168°28'	5182	63
SOTWX 1FFA	7°16'	168°29'	5668	64
SOTWX 5FFA	7°29'	168°29'	5619	65
SOTWX 4FF	8°17'	168°31'	4565	66
CATO 10*	7°31'	168°49'	5288	67
CATO 28*	7°24'	168°33'	5471	68
PROA 116	8°49'	168°33'	4550	69
STYX4 11	7°40'	168°33'	5423	70
CHAIN 100M	8°19'	168°33'	4482	71
CATO 33	7°45'	168°33'	4700	72
CHAIN 100F-J	8°46'	168°40'	4800	73
SOTWX 3FFA	8°31'	168°43'	5145	74
CHAIN 100 B-D	8°20'	168°47'	4891	75
STYX4 10	8°45'	168°55'	5021	76
RC12 20	9°25'	169°00'	5291	77
STYX4 7	9°37'	170°37'	4162	78
STYX4 12	7°41'	170°51'	5440	79
VIT 3802	3°17'	172°52'	5329	80
MEND 607	13°50'	145°25'	5147	81
RC11 D22	12°52'	145°33'	4662	82
SHIMA 122	11°01'	146°02'	4934	83
AMPH 117P	12°24'	148°24'	5151	84
AMPH 116G	11°26'	149°17'	5106	85
AMPH 116	11°26'	149°17'	5106	86
CM2 14	13°34'	149°18'	4520	87
CHAL 276	13°28'	149°30'	4310	88
V18 32	14°18'	149°32'	2008	89
V18 29	14°29'	150°01'	1789	90
V18 30	14°29'	150°01'	1175	91
CM 9	13°50'	150°33'	?	92
CM10	13°55'	150°33'		93
MSN 128G	13°53'	150°35'	3623	94
MERO 2P50	13°53'	150°35'	3695	95
CM2 11	14°05'	150°38'	3760	96
TF 2	13°53'	150°38'	3623	97
CM 15	13°20'	150°39'	?	98

TABLE I (Cont.)

Station	Position		Depth(m)	Identification on sample location map
	S	W		
RC13 73	12°38'	150°46'	4784	99
RC13 72	11°56'	150°56'	4980	100
VIT 5982	14°19'	153°08'	4910	101
VIT 5110	12°59'	154°07'	5222	102
V18 BBD1	14°02'	155°09'	5012	103
VIT 6332	13°02'	160°30'	5060	104
V18 279	12°42'	160°37'	4753	105
V18 280	12°27'	159°23'	4989	106
VIT 6333	12°55'	160°44'	4300	107
V18 277	12°42'	160°45'	3952	108
V18 276	12°42'	160°49'	3587	109
AMPH 80	11°51'	160°51'	3803	110
V18 274	12°45'	160°56'	3500	111
V18 275	12°44'	160°56'	3623	112
V18 270	12°15'	160°57'	2520	113
V18 267	12°17'	161°03'	2760	114
I165A 2	14°14'	165°39'	5551	115
I160A 1	12°21'	168°33'	5404	116
I160A 2	12°22'	168°33'	5403	117
STYX9 02BX	11°55'	169°32'	?	118
2P 51	9°52'	145°56'	4900	119
MSN 139D	0°04'	147°36'	3340	120
CNEXO A3	3°14'	148°09'	4800	121
CNEXO A4	2°37'	148°09'	4765	122
CNEXO A2	3°57'	148°18'	4735	123
CNEXO A1	4°37'	148°20'	4755	124
RC13 70	9°42'	151°24'	4803	125
RC13 66	4°49'	152°38'	5332	126
CHAL 274	7°25'	152°15'	5033	127
M70 028	7°40'	161°37'	4540	128
R12 87	2°18'	163°58'	5243	129
SOTW 680	9°48'	164°45'	4199	130
STYX 80	3°48'	166°06'	?	131
STYX 72	"	"	5217	132
STYX 81FF43	"	"	?	133
STYX 81FF42	"	"	?	134
STYX9 03BX	8°01'	166°35'	?	135