The distribution of rare earth, precious metal and other trace elements in Recent and fossil deep-sea manganese nodules

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(Received March 1, 1978; accepted in revised form August 22, 1978)

Four deep-sea manganese nodules and one fossil nodule from Timor have been analysed for 45 elements (major elements, rare earths and precious metals) by X-ray fluorescence, spark source mass spectrometry and neutron activation analysis. Co-existing sediments from two nodule sites in the Southwestern Pacific Basin have also been analysed. Differences in nodule composition are apparent, particularly for the Timor nodule. The trace metal compositions of this nodule, however, reveals it to be a typical deep-sea nodule, although some element redistribution has clearly taken place since exposure of the nodule on land. The distribution of a number of elements including Tl, Ir, Pd, Au and the rare earth elements between deep-sea nodules and their associated sediments appears to be dependent on a number of factors including the major element composition of the nodule (e.g. dilution by the silicate phase of the nodule), the differing stability of various element complexes in seawater, and the influence of differences in redox states on complex stability. Au and Si, on the other hand, are positively correlated in nodules and sediments possibly because they have a common source, either submarine detritus or basalt-seawater interaction. The rare earth contents of the sediments from the N.E. sector of the Southwestern Pacific Basin are high compared with previous determinations of rare earths in marine sediments and show no evidence of Ce depletion relative to La on a shale-normalised basis. These high contents reflect the well oxidised conditions and low sedimentation rates of this environment.

INTRODUCTION

Although the distribution of trace elements, and in particular the rare earth elements, in marine manganese nodules has received considerable attention (e.g. HERRMANN 1970; PIPER 1972, 1973, 1974a, b; CROCKET *et al.* 1973; GLASBY 1973, 1975; VOLKOV and FOMINA 1973; BALASHOV *et al.* 1974; SHIMA 1974; FLEET 1975; MASUDA and NAGASAWA 1975; SUGIMURA *et al.* 1975; SUGIMURA 1977; RANKIN and GLASBY *in press*), the time consuming nature of the analytical techniques has resulted in only a limited number of analyses being available. Consequently, there is little consensus as to the mode of incorporation of trace elements in manganese nodules.

In this paper, we report the results of the analysis of four deep-sea manganese nodules for 45 elements using spark source mass spectrometry, neutron activation analysis and X-ray fluorescence spectroscopy. The major and trace

element data are compared with those obtained from a fossil manganese nodule from Timor, believed to have been formed in a deep-sea environment. In addition, co-existing sediments from two sites in the Southwestern Pacific Basin have been analysed in order to show the relationship between the distribution of trace elements in deep-sea manganese nodules and their underlying sediments.

SAMPLE LOCATION AND DESCRIPTION

Five manganese nodules from a range of deep-sea and fossil environments were selected for this study. Summaries of sample locations, sample descriptions, associated sediment types, nodule mineralogy and previous element analyses have been given by JOHNSTON and GLASBY (1978, Table 1). An account of the iron oxide mineralogy of the nodules has also been presented by JOHNSTON and GLASBY (1978).

Nodule samples G994 and G1004c were col-

Table 1. Major and minor element composition of 5 nodules and 2 sediments. All analyses in percent. Element analyses by X-ray fluorescence spectroscopy.

	Nodules				Sediments						Average Pacific Pelagic Clay (1)
	G994	G1004c	6269	Z2140c	Timor	G994		G1003		Dome Site C Average (1)	
						Washed	Unwashed	Washed	Unwashed		
Fe ₂ O ₃	25.06	21.36	27.62	16.79	25.22	10.00	9.43	10.97	10.36	7.64	8.2
MnO	21.95	26.33	23.15	23.42	13.64	1.50	1.27	1.98	1.67	1.57	2.55
SiO ₂	15.77	14.15	17.88	28.90	32.80	46.57	41.70	45.45	40.92	50.11	56.5
Al ₂ O ₃	6.25	6.00	3.28	3.34	5.97	14.84	13.18	14.71	13.26	14.22	15.6
TiO ₂	2.28	1.81	1.00	0.88	0.90	0.82	0.71	1.02	0.88	0.71	0.64
CaO	2.78	2.71	2.76	2.46	2.77	8.42	7.59	7.71	6.98	2.59	0.86
K ₂ O	0.50	0.75	0.88	1.16	0.61	2.18	2.01	2.34	2.13	3.15	2.5
P ₂ O ₅	0.74	0.65	0.66	0.26	0.61	0.50	0.44	0.86	0.71	0.39	0.16
MgO	2.59	2.96	2.25	3.07	2.13	3.42	3.47	3.42	3.30	3.24	3.4
SO ₃	0.51	0.45	0.88	0.25	0.09	0.38	—	0.38	—	—	—
Na ₂ O	1.26	1.21	1.16	1.61	0.34	1.59	2.61	1.58	2.72	2.91	1.7
Cu	0.28	0.37	0.15	0.37	0.28	—	—	—	—	0.083	0.034
Ni	0.43	0.76	0.46	0.85	0.38	—	—	—	—	0.05	0.02
Cr	—	—	0.002	0.004	0.002	—	—	—	—	0.014	0.009
Co	0.42	0.38	0.08	0.06	0.08	—	—	—	—	—	—
Cl	1.10	0.92	0.65	1.06	0.06	0.3	—	0.3	—	—	—
CO ₂	—	—	—	—	—	3.31	—	3.42	—	—	—
H ₂ O ⁺	—	—	—	—	—	7.03	—	7.07	—	—	—
Ign. loss	16.17	15.93	13.57	12.43	15.52	9.64	10.27	9.45	10.13	—	—
Total	98.39	96.74	96.43	96.91	101.38	99.86	92.68	99.49	93.07	—	—

(1) from BISCHOFF and PIPER (1976) (see BISCHOFF and PIPER (1977) for comparison).

lected in the N.E. sector of the Southwestern Pacific Basin in the vicinity of Rarotonga during the cruise of R.V. *Tangaroa* in May 1974 (see MEYLAN *et al.*, 1975; BÄCKER *et al.*, 1976). Both sites are characterised by high nodule densities and greyish brown clay (5YR 3/2) sediments. A sediment sample from Stn G994 was analysed. Because no sediment was collected at Stn G1004c, sediment from Stn G1003, 92km away, was analysed instead. Although both sediments are pelagic clays, they contain significant quantities of carbonate (Table 1).

Nodule sample 6269 was collected on the western flanks of the Carlsberg Ridge, Indian Ocean, during the cruise of the R.R.S. *Discovery* in 1967 (GLASBY *et al.*, 1974). The dominant sediment type is globigerina ooze.

Sample Z2140 was collected at Stn 39 during cruise 36 of U.S.N.S. *Eltanin* in November 1969 (GLASBY, 1972a). The haul consisted mainly of nodules showing a wide range of morphologies and containing highly weathered volcanic cores. Manganese crustal thickness was generally of the order of 1mm. Glacial erratics also occurred as nodule nuclei. No sediment was recovered at this station.

The fossil manganese nodule from western Timor occurs on the Bobonaro Scaly Clay olistostrome (AUDLEY-CHARLES, 1972). It is believed to have formed during the Cretaceous in a deep-sea environment on red clay and uplifted during the Miocene (MARGOLIS *et al.*, 1978).

ANALYTICAL TECHNIQUES

Samples were prepared for analysis by grinding the material finely with a pestle in a porcelain mortar. Bulk samples were used for the two sediment samples and for nodule samples G994, G1004c and 6269. For Z2140, where the nodules had only a thin coating of manganese oxide around a nucleus of other material, hand picking of the outer crust was necessary. The fossil Timor nodule contained a hard, inner volcanic core which was removed during sample preparation.

No attempt was made in this study to investigate variations in composition between nodules from the same site or within individual nodules (e.g. RAAB, 1972).

The sediment samples contained approximately eight percent water-soluble salts. The samples were analysed after being washed in distilled water for 24 hours. For comparison

unwashed sediment samples were also analysed for major elements (see Table 1).

1. *X-ray fluorescence analysis* Fe, Mn, Si, Al, Ti, Ca, K, P, Mg, S were determined at the University of Melbourne in fused discs with a Siemens XRF spectrometer using the method described by NORRISH and HUTTON (1969) and THOMAS and HAUKKA (1978). Na and Cl were also determined by XRF but in pressed powder discs. The samples were subsequently re-analysed at Soil Bureau, D.S.I.R., and concordant results were obtained.

2. *Neutron activation analysis* Pd, Au, Ir, Tl, Cr and Co were determined by a neutron activation analysis scheme modified from that of CROCKET *et al.* (1968) and KEAYS *et al.* (1974). The accuracy of the data is within $\pm 15\%$; results by this method are compared with published data by SHAW *et al.* (1976). Re was also determined by neutron activation analysis using a method described by LOVERING and BUTTERFIELD (1970).

3. *Spark source mass spectrometry* The samples were mixed with an equal weight of ultra pure graphite containing 500ppm lutetium oxide as an internal standard. The concentration of 24 elements, including the rare earth elements, were determined. Details of the analytical technique are reported in RANKIN and CHILDS (1976). The mass spectrometric data is considered to have a precision of $\pm 15\%$ (based on repeat analyses of the USGS standard BCR-1).

Fig. 1-a.

Fig. 1-b.

Fig. 1. Shale-normalised rare earth data for 5 marine nodules and 2 sediments. Shale data taken from HASKIN and SCHMITT (1967). Data supplied by P. J. POTTS (Open University) are neutron activation analyses of a replicate sample of the Timor nodule analysed for this paper by mass spectrometry. Data supplied by A. J. FLEET (Open University) are neutron activation analyses of a second Timor nodule from the Bobonaro Scaly clay olistostrome collected independently from the nodule described here.

(The fossil Timor nodule was also analysed for some rare earth elements by neutron activation analysis (P. J. POTTS, pers. comm.). These were obtained to provide an assessment of the rare earth element data obtained by the spark source mass spectrometric technique; see Fig. 1).

4. *Other analyses* Cu and Ni were measured using a Varian Techtron (model AA-3) atomic adsorption spectrometer.

Whole sample H_2O^+ was determined by heating the dried ($110^\circ C$) samples at $1,200^\circ C$ in an oxygen stream and absorbing the liberated H_2O onto magnesium perchlorate. Total CO_2 measurements were made by the Leco gasometric technique.

RESULTS

A. Nodules

Major and minor element chemistry The similarities in the trace element chemistry of nodules G994 and G1004c from the Southwestern Pacific Basin (Table 2) are probably a reflection of the similarities in their major element compositions (Table 1). Most analyses lie within 15% of each other which represents good agreement considering the sampling problems involved in the analysis of manganese nodules. The major element data are similar to those in sample 6269. By contrast, sample Z2140 contains up to a factor of two less of a

range of trace elements, although Cs is higher in this sample. Although the reasons for the difference in major element composition of Z2140 from the other three deep-sea nodules are not understood, it may in part be related to the higher content of silicate minerals in the sample (possibly due to inclusion of nucleus material during sample preparation, as revealed by higher concentration of SiO_2 , although Al_2O_3 is lower in this sample). Cs would be associated with the silicate phases and this is at a higher concentration in sample Z2140. Inclusion of extraneous silicate material would have the effect of lowering relatively the contents of authigenic elements in the sample.

The fossil Timor nodule shows a number of differences in composition from the deep-sea nodules. In particular, it has significantly higher contents of Th, Pb and Hf and lower contents of U and Y. These differences may reflect in part diagenetic changes due to weathering on land (c.f. MARGOLIS *et al.* 1978; JOHNSTON and GLASBY, 1978). The overall composition of the Timor nodule reveals it to be of deep-sea origin.

Rare earth elements The results presented in Table 2 indicate a close similarity in absolute rare earth abundances in nodules from the Southwestern Pacific Basin (G994 and G1004c), where red clays form the dominant sediment type, and the nodule from the Carlsberg Ridge, Indian Ocean (6269), where globigerina ooze is the dominant sediment. Sample Z2140 (Indian-Antarctic Ridge) is up to a factor of two lower in concentration of individual rare earths while the fossil Timor nodule is a factor of two to seven lower in concentration of rare earth elements compared to nodules G994 and G1004c.

The concentrations of the rare earth elements agree well with those obtained by previous authors (e.g. VOLKOV and FOMINA 1973; PIPER 1974a).

Figure 1 shows the shale-normalised rare earth abundance patterns of five manganese nodules obtained following the method of RANKIN and CHILDS (1976). The data for the average deep-sea nodule of PIPER (1974a, b) are plotted for comparison. The 4 deep-sea nodules (G994, G1004c, 6269 and Z2140) show similar trends. Cerium exhibits its well known enrichment relative to the neighbouring rare earth elements, reflecting its oxidation in nodules to its tetravalent state (GOLDBERG *et al.* 1963; GLASBY 1973). The rare earth element data are also

Table 2. Trace element composition of 5 marine nodules and 2 sediments. All analyses in ppm, except where otherwise stated.

	Nodules					Sediments		BCR-1	
	G994	G1004c	6269	Z2140	Timor	G994	G1003	This Work	FLANAGAN (1973)*
Yb	22	22	19	9.6	5.9	8.3	14	3.6	[3.36]
Er	23	23	21	10	6.2	8.7	15	3.3	3.59
Ho	8.1	7.7	7.7	3.9	1.8	3.3	6.2	1.2	(1.2)
Dy	34	33	34	17	—	14	24	6.3	6.3
Tb	6.0	5.5	5.8	3.6	—	2.3	4.1	0.96	1.0
Gd	33	37	37	24	—	14	24	6.5	6.6
Eu	10	9.6	12	7.2	1.8	3.2	6.0	2.2	1.94
Sm	43	40	51	28	4.6	13	26	6.4	6.6
Nd	170	140	190	110	22	63	88	28	29
Pr	43	33	47	26	4.4	14	21	6.9	(7)
Ce	>200	>200	>200	>200	>200	>200	>200	53	53.9
La	180	130	180	86	34	76	64	24	[26]
U	5.8	6.4	7.2	3.4	2.6	1.7	2.4	1.7	(1.74)
Th	33	30	35	30	97	17	23	5.6	6.0
Pb	>100	100	>100	60	>100	60	63	21	(17.6)
Hf	9.8	8.4	9.3	6.1	12	2.8	4.7	3.8	[4.7]
Ba	>1000	>1000	>1000	>1000	>1000	>1000	640	800	675
Cs	0.86	0.78	0.60	1.3	0.86	4.4	3.5	1.6	0.95
Sn	6.0	5.3	2.7	2.7	5.3	2.2	3.3	—	—
Nb	>30	>30	>30	>30	>30	10	17	13	13.5
Zr	>300	>300	>300	>300	>300	150	150	220	(190)
Y	>100	>100	>100	63	35	>100	>100	44	[37.1]
As	>50	>50	>50	>50	>50	>50	>50	—	—
Sr	>700	>700	>700	>700	>700	450	250	—	—
Tl	144	160*	59*	64.2	27.7	1.98*	2.78*	—	—
Pd(ppb)	7.2	6.5	6.4	20.9	5.3	10	14	—	—
Au(ppb)	0.16	0.13	0.28*	0.84	0.18	2.21	1.15	—	—
Ir(ppb)	3.62	4.3*	2.57*	1.38	7.76	0.5	0.45	—	—
Re(ppb)	<0.19	<0.10	<0.06	0.05	<0.14	—	—	—	—

* [] = average; () = magnitude; — = recommended.

* Duplicate analyses.

plotted relative to the rare earth data for seawater (GOLDBERG 1965) in Fig. 2. This distribution pattern is similar to that observed by GLASBY (1973) and PIPER (1974a), i.e. with the exception of Ce, there is a decrease in rare earth content relative to seawater with increasing atomic number.

The neutron activation rare earth data obtained for the fossil Timor nodule (P. J. PORTS, pers. comm.), while differing in absolute concentration from the mass spectrometric data, show a similar distribution pattern relative to shale (Fig. 1). Also included in Fig. 1 are data from A. J. FLEET (pers. comm.) for another sample of a fossil Timor nodule.

Precious metals Analytical results for Pd, Au and Ir are presented in Table 2 and are compared with published data for hydrogenous nodules in Table 3. Although the averages for the manganese nodules for Au and Ir are con-

Fig. 2. Rare earth element distribution in nodules relative to mean abundance in seawater (GOLDBERG 1965). Ordinate scale should be multiplied by 10^6 . Note that there are considerable differences in the rare earth concentrations of seawater reported by GOLDBERG (1965) and PIPER (1974a) (see also MARTIN et al. 1976).

Table 3. Comparison of precious metal data for marine nodules and sediments. All analyses in ppb.

Deep-sea hydrogenous manganese nodules			
Ir	Pd	Au	Reference
9.5(16)*	5.3(19)	2.9(19)	HARRISS <i>et al.</i> (1968)
0.9–23.1 [†]	0.24–9.25	0.21–8.28	
7.8(1)	—	0.36(1)	KEAYS and SCOTT (1976)
2.97(4)	6.7(3)	0.35(4)	This work
1.38–4.31	6.4–7.2	0.13–0.84	
7.41(21)	5.49(22)	2.37(24)	Grand Average
Deep-sea sediments			
0.35(3)	4.5(21)	2.7(21)	CROCKET <i>et al.</i> (1973)
0.15–0.47	0.7–13.3	0.64–5.6	
0.21(21)	—	—	BARKER and ANDERS (1968)
0.47(2)	12.0(2)	1.68(2)	This work
0.25(26)	5.15(23)	2.61(23)	Grand Average
Fresh water manganese concretions			
<0.1	0.045(2)	0.38(2)	HARRISS <i>et al.</i> (1968)

* Number of analyses in arithmetic mean given in parentheses.

† Range of values.

siderably lower than those of HARRISS *et al.* (1968), the data for the 3 precious metals fall within the range of concentrations observed by HARRISS *et al.* (1968). The results for Pd, Au and Ir in the deep-sea nodules are approximately three orders of magnitude lower than those previously reported for Hawaiian manganese crusts (ANON 1974) and this suggests that these previous analyses for the Hawaiian crusts, with their economic implications, are in error. This has been confirmed by J. L. BISCHOFF (pers. comm.). Similarly, analyses of Pd and Au in nodules reported by RANKAMA and SAHAMA (1950, pp. 694 and 707) and by SHILO *et al.* (1977) are much too high (see also NOAKES and JONES 1975, p. 1102 for comments on Pt values). The precious metal concentrations in the fossil Timor nodule confirm that it was of deep-sea origin as suggested by MARGOLIS *et al.* (1978). The nodules have much higher Pd and Ir contents than freshwater manganese nodules (HARRISS *et al.* 1968) and their Ir contents are greater than most crustal rocks (CROCKET 1969; CROCKET and TERUTA 1977).

The Au contents of the nodules correlate positively and the Ir contents negatively with their silica contents (Figs. 6 and 7).

Thallium The average Tl content of the 4 deep-sea nodules (106ppm) agrees well with

the average value (100ppm) reported by DE ALBUQUERQUE and SHAW (1972). The Tl content of the nodules decreases with increasing silica content. The two nodules from the South-western Pacific Basin (G994 and G1004c) have the lowest SiO₂ contents and the highest Tl concentrations.

B. Sediments

In an attempt to establish the relationship of the composition of manganese nodules to that of the underlying sediment, two sediment samples (G994 and G1003) from the South-western Pacific Basin were analysed. As noted earlier, because of the proximity of Stn G1003 to Stn G1004C, nodules from G1004c and sediment from G1003 were regarded as being from the same station.

The two sediment samples are similar in composition (Tables 1, 2), although G1003 is slightly higher in all elements except Si, Ca, Mg, La, Sr, Cs, Ba and Au. The higher contents of Si, Sr and Ba in G994 may be related to higher contents of terrigenous material derived from the New Zealand landmass as this sample was taken from a station closer to New Zealand than G1003 (see MEYLAN *et al.* 1975; BÄCKER *et al.* 1976 for discussions). Dilution by terrigenous material would have the effect of lowering the relative concentrations of elements derived from

other sources and could therefore account for their lower observed value in sample G994. The reasons for the higher values of La and Au are not known. The sediments are similar in composition to previously reported averages for DOMES Site C in the Northeast Equatorial Pacific and of the whole Pacific (BISCHOFF and PIPER 1976). Minor differences that are observed are probably due to differences in relative amounts of silicate, carbonate and authigenic phases. For G994 and G1003 sediments, the Au values are similar to those reported for sediments from the flanks of the East Pacific Rise (CROCKET *et al.* 1973; PIPER and GRAEF 1974). The rare earth element concentrations are, however, higher than those in a number of abyssal marine and other sediments (HASKIN and GEHL 1962; WILDEMAN and HASKIN 1965; HASKIN *et al.* 1966; SHIMOKAWA *et al.* 1972; VOLKOV and FOMINA 1973; FLEET and KEMPE 1974; PIPER 1974b; PIPER and GRAEF 1974; PIPER *et al.* 1975; FLEET 1977; HEIN *et al.* In press; MELGUEN *et al.* In press) as well as in marine basalts (MASUDA and NAGASAWA 1975; FLEET *et al.* 1976; THOMPSON *et al.* 1978), although the La concentrations are lower than those reported in previous spectrographic analyses of some marine clays (YOUNG 1954; GOLDBERG and ARRHENIUS 1958; EL WAKEEL and RILEY 1961) (see however, DYMOND *et al.* 1973, 1977). The high rare earth contents of the G994 and G1003 sediments therefore probably reflect the well oxidised nature of these sediments (to be published elsewhere). Further, there appears to be no evidence of Ce depletion relative to La on a shale-normalised basis in these sediments as noted by PIPER (1974b) for other marine sediments suggesting that Ce depletion is not a characteristics of all marine sediments, particularly ones from well oxidised, low sedimentation rate environments such as encountered in the N.E. sector of the Southwestern Pacific Basin.

C. Element enrichment sequence

For Stn G994 the enrichment sequence of elements in nodules relative to the surrounding sediment is as follows (enrichment values given in parentheses):

Tl(73) > Mn(17) > Ir(7.4) > Hf(3.5) > U(3.4)
 > Ti(3.2) > Fe(2.7) = Sn(2.7) > Yb(2.6)
 > La(2.4) > Th(1.9) > P(1.7) > Mg(0.75)
 > Pd(0.72) > Na(0.48) > Al(0.47) > K(0.40)
 > Si(0.38) > Ca(0.37) > Cs(0.20) > Au(0.07)

Elements not included in the above sequence because the element concentration data for the nodule are quoted as "greater than" are Nb(>3), Zr(>2), Pb(>1.7) and Sr(>1.5).

This element enrichment sequence is very similar to that observed for the G1004c nodule/G1003 sediment pair (although the enrichment values are slightly different due chiefly to the different sediment composition). In addition, the sequence is not too dissimilar from those calculated from the data of LANDMESSER *et al.* (1976) and CALVERT and PRICE (1977) or of BONATTI *et al.* (1971) for elements enriched by diagenesis in the upper layers of sediment cores relative to lower horizons. Differences indicate that this sequence is, however, not uniform from place to place.

A striking feature of the element enrichment sequence is the marked enrichment of Tl in the nodules relative to surrounding sediment. The alkali metals and alkaline earths, the elements associated with the silicate phase, together with Pd and Au, on the other hand, constitute the elements least enriched in nodules relative to sediments. It is interesting that the two noble metals, Au and Ir, lie at either end of the enrichment sequence; this may be due to their markedly different abilities to form complexes and the relative stabilities of these complexes in different redox environments.

Comparison of the rare earth distribution in nodules with that in the underlying sediments (Fig. 1) shows that nodules at Stn 994 has higher rare earth element enrichment than that observed at Stn G1004c. This may be due to the fact that while the rare earth contents of the nodules are relatively constant throughout the Southwestern Pacific Basin, sediment composition is affected by the input of terrigenous sediment as discussed previously. This would have the effect of decreasing the rare earth contents of nodules relative to sediments in the Southwestern Pacific Basin with increasing distance from the New Zealand landmass. Alternatively, the sediments may contain differing proportions of micromnodules. The presence of micromnodules in sediments would decrease the observed rare earth element enrichment. The similarity of the shape of the shale-normalised curves for nodules and sediments suggests the possibility of incorporation of ferromanganese material.

DISCUSSION

A striking feature of the data is the similarity in trace element concentrations in nodules from two sites 258 km apart in the Southwestern Pacific Basin. This suggests that variations in trace element compositions of nodules within individual deep-sea basins are likely to be small where sediment composition changes are not marked. Future studies of such variations should therefore only be carried out using very precise analytical techniques. The similarity in trace element composition of the nodules in this basin is probably a reflection of their major element composition. In addition, the similarity in composition of nodules from the Southwestern Pacific Basin where red clay is the dominant sediment type to the nodules (6269) from the Carlsberg Ridge, Indian Ocean, where globigerina ooze is the dominant sediment type, suggests that sediment type *per se* is not the major factor controlling the trace element composition of deep-sea nodules. Since all samples studied here contain δMnO_2 as the principal manganese oxide material, manganese oxide mineralogy is clearly not a major factor in controlling difference in composition of these nodules (c.f. CALVERT and PRICE 1977; CALVERT *et al.* 1978). However, the higher silicate mineral content of Z2140 from north of the Indian-Antarctic Ridge may explain the lower rare earth element abundance of this particular nodule. A further factor controlling the content of trace elements in nodules is nodule growth rate (e.g. HEYE and MARCHIG 1977; PIPER and WILLIAMSON 1977). PIPER and WILLIAMSON (1977), for example, have shown that Mn/Fe ratios of nodules are related to nodule growth rate. However, the four deep-sea nodules studied in this paper all have Mn/Fe ratios close to unity (with a range of 1.7) which in some cases is somewhat less than that shown by the minor elements. This suggests that variations in nodule growth rate are not the only factor in controlling trace element composition.

The relationship between the element concentration in nodules and their underlying sediments is very similar for Stns G994 and G1004c. This relationship is linear (Fig. 3) as has been shown by GLASBY (1975) using mean data from diverse sources in the literature (GLASBY 1975, p.134 Fig. 2). Several other authors have also pointed to a relationship between the element composition of deep-sea manganese nodules and their associated pelagic sediments (e.g. RILEY and CHESTER 1971; ELDERFIELD 1972; CHESTER *et al.* 1973; see also CHESTER and ASTON 1976;

Fig. 3. Relationship between element composition of nodule and the underlying sediment at Station G994.

ELDERFIELD 1976). The trend reported here supports the idea of a similar mode of incorporation of elements into manganese nodules and their associated sediments in a region as the Southwestern Pacific Basin where red clay forms the dominant sediment type. The enrichment sequence of elements shows that Tl is the most enriched in nodules relative to the underlying sediment (also noted by GLASBY, 1975) and Cs and Au are the least enriched, possibly because of their association with clay minerals in the marine sediments.

The fossil nodule from Timor appears to be anomalous in composition. Weathering during the extremely long period of exposure on land may have resulted in some loss of the more mobile elements from the nodule. This view is supported by the recent work of JOHNSTON and GLASBY (1978) using Mössbauer spectroscopy which has shown that recrystallisation of the iron oxide phase of the Timor nodule has taken place since the nodule was exposed and this may have led to some element redistribution. In spite of this, the trace element composition can be recognised as being typical of that of a deep-sea nodule.

Few studies have been made on the variation of rare earth elements in nodules within a given ocean. In a publication by VOLKOV and FOMINA (1973), it was established that the total rare earth content of Pacific Ocean nodules increases with increasing distance from land and is correlated with the iron and manganese contents of the nodules (c.f. VOLKOV *et al.* 1975). Replott-

Fig. 4. Relationship in deep-sea nodules of La content (representing total rare earth content) and geographic location of station from which nodules were obtained (data from PIPER 1974a).

ing the La contents (as a measure of Σ R.E.E.) of Pacific Ocean nodules obtained by PIPER (1974) on a geographic basis (Fig. 4) lends some support to this observation; lowest La values (in the range 100–200 ppm) are found at the margins of the Pacific Basin whilst highest values (up to 500 ppm) are found in the deep-ocean basins far from land. The data of SHIMOKAWA *et al.* (1972) show similar features. This trend is, however, not entirely consistent and there appears to be no direct correlation of the La content with water depth in Pacific Ocean nodules (Fig. 5) indicating that depth *per se* is not a major factor in controlling the total rare earth content in nodules. By contrast, a relationship between the U and Th contents of manganese nodules and water depth has been suggested by a number of workers (e.g. KU and BROECKER 1969; MO *et al.* 1973; MARGOLIS *et al.* 1978) (see also SUGIMURA *et al.* 1975; KUNZENDORF and FRIEDRICH 1976a, b, 1977; KORKISCH *et al.* 1977). The nodules analysed here display U and Th values typical of those obtained for deep-sea nodules by these authors. The U and Th concentrations of marine sediments and basalts have been presented by HEYE (1969), BOSTRÖM and FISHER (1971), TUREKIAN and BERTINE (1971), MACDOUGALL (1977) and MITCHELL and AUMENTO (1977). The origin of

the geographic variation in the total rare earth contents of Pacific Ocean nodules is not understood but may be related to diagenetic processes similar to those outlined by PRICE and CALVERT (1970), HORN *et al.* (1972) and GLASBY (1975) (c.f. CALVERT and PRICE 1977; PIPER and WILLIAMSON 1977; CALVERT *et al.* 1978). It should be emphasised, however, that whilst VOLKOV and FOMINA (1973) found a relationship between the total rare earth contents of Pacific Ocean nodules and the manganese and iron contents of the nodules, no similar correlation between the rare earth element content and either the manganese or iron contents was found in the 5 nodules studied in this paper. RANKIN and CHILDS (1976) found a positive correlation between the total rare earth element content and Mn (but not Fe) for nodules formed in New Zealand soils.

The distribution of Tl, Ir, Pd and rare earth elements between deep-sea manganese nodules and their associated sediments appears to be strongly influenced by a number of factors, including the major element composition of the nodules, the differing stability of the various complexes of the elements, and the difference in redox state between the nodules and the sediments.

The silica contents of the nodules would

Fig. 5. Relationship in deep-sea nodules of La content (representing total rare earth content) and depth (data from PIPER 1974a).

appear to be particularly important in the control of the distribution of Tl, Ir, Pd and rare earths. This contradicts the observations of HARRISS *et al.* (1968) that no correlation exists between variations in the precious metal and major element content. A positive relationship between Au and silica for both nodules and associated sediments is suggested by Fig. 6 and this can be interpreted to indicate that Au is not adsorbed onto authigenic ferromanganese oxide phases but is incorporated with the detrital silicate minerals and authigenic clays. This interpretation is supported by the fact that the two red clay sediments (G994, G1003) contain a factor of ten more Au than the associated nodules (Table 2). CROCKET *et al.* (1973) have argued that the detritus contributed to the marine environment will not differ in Au, Pd or Ir content compared to its continental source

Fig. 6. Positive correlation between the Au and SiO_2 contents of deep-sea nodules and red clay sediments. The dashed line represents a mixing curve between detritus containing 17ppb Au (the average Au content of the sediments) and an authigenic Fe-Mn component containing no Au or SiO_2 . Note that all of the nodules contain significantly less Au than that which they would have contained if formed by simple mixing of these two end members. The low Au content of the Timor nodule suggests that it contained much less silica before obduction.

rocks, and some of the Au will therefore be incorporated in the detrital material. If the detrital material in the nodules contributed the same amount of Au to the nodules as it does to the underlying sediments (average Au content = 1.7ppb) and if its silica content is the same as that of the sediments, then it should be possible to calculate the amount of Au contributed to the nodules by the detrital material. Clearly, the nodules contain much less Au than that which would have been contributed by detritus (Fig. 6). In the case of nodule G994 with a silica content of 15.8%, 0.64ppb Au would have been contributed by detritus whereas the nodule contains only 0.16ppb Au. Hence, 0.48ppb Au is unaccounted for in the nodule. The explanation may be that some of the Au contributed with the detritus (perhaps Au contributed by organic particles which are believed by HUMMEL (1957) to be a significant carriers of Au in the marine environment) was solubilized in the environment of the manganese nodules.

Gold contributed by detritus to the deep-sea sediments will encounter a low redox environment (Eh c.0.05v) at a depth of 50cm whereas that contributed to the manganese nodules will be subjected to a much higher oxidation poten-

tional (Eh in excess of 0.65 and possibly as high as 0.80v) (CRERAR and BARNES 1974). Gold contributed to the sediments is likely to remain as a solid, probably metallic Au, while part of that added to the nodules may form complex ions. At a pH of 7.5, the approximate pH of deep ocean waters (PARK 1968), AuCl_4^- is the most stable complex of Au in seawater (BAES and MESMER 1976) (cf. CROCKET 1974). Gold leached from the manganese nodule as AuCl_4^- (or any other complex ion) may then be added either to the surrounding seawater or to the underlying sediments where it would precipitated because of their low redox state.

The Timor nodule is anomalous in the relationship between Au and silica contents (Fig. 6). Its Au content (and its high Ir content) would suggest that the nodule originally contained less than 16% SiO_2 . This agrees with the findings of MARGOLIS *et al.* (1978) that the present high silica content (33%) may reflect the diagenetic loss of manganese from the nodule during exposure on land.

The inverse correlations of Ir, Tl and the rare earths with silica content (see Fig. 7 for Ir/silica data) can be explained to different degrees by

Fig. 7. Negative correlation between Ir and silica contents of deep-sea nodules and red clay sediments. The high Ir content of the Timor nodule confirms that it is an obducted deep-sea nodule that originally contained about 15wt. per cent silica.

dilution of the ferromanganese oxide phase by silicate minerals. Most of the variations in the rare earth contents of the nodules can be interpreted in terms of simple dilution by silicate minerals. The rare earths are preferentially incorporated into the nodules due to hydrolysis under oxidising conditions. Dilution by silicates does not account for all the variation observed in the content of Ir and Tl. An additional factor in the case of Ir may be the growth rate of the nodules while the marked variation of Tl with silica content may be influenced by variations in redox state. Tl^+ is stable in acid and alkaline aqueous solutions whereas Tl^{3+} is stable only in solutions of low pH, forming the very insoluble thallic hydroxide precipitate when solutions of Tl^{3+} are made basic (PETERSON 1962). It is therefore possible that Tl goes into solution as Tl^+ in the low oxidizing environment of the sediments whereas in the ferromanganese nodules it is oxidized to Tl^{3+} and precipitated as $\text{Tl}(\text{OH})_3$.

The reason for the low enrichment of many elements in the nodules relative to the sediments may be the ability of the elements to form stable complexes in seawater which inhibit the incorporation of these elements into the nodules. In the case of Au it may be chloro complexes, as stated above, whereas carbonate complexes may be important in the case of U and Pb (see (AHLAND 1975; BREWER 1975; STUMM and BRAUNER 1975; LONG and ANGINO 1977; VAN DER WEIJDEN and KRUSSINK 1977). Among the elements most enriched in nodules relative to sediments, Tl, Zr, Th, Ti and Sn exist in the forms Tl^+ , $\text{Zr}(\text{OH})_4^0$, $\text{Th}(\text{OH})_4^0$, $\text{Ti}(\text{OH})_4^0$ and $\text{SnO}(\text{OH})_3^-$ respectively (BREWER 1975). From the data of LANDMESSER *et al.* (1976), niobium (which is probably present in seawater in the particulate form), molybdenum (MoO_4^{2-}), and tungsten (WO_4^{2-}) are in this category (BAES and MESMER 1976, p.249). It therefore appears that complex formation in the seawater has a marked effect in controlling the enrichment of elements in nodules by inhibiting adsorption or coprecipitation of complexed species. The low contents of Re and Cr in nodules may, however, reflect formation of stable anionic species in this seawater (GLASBY 1973) which may not be readily taken up into nodules.

Acknowledgements—Mr. M. T. HAUKKA (University of Melbourne) is thanked for the X.R.F. determinations; these were subsequently confirmed by Mr. J. L. HUNT (Soil Bureau). Mr. P. HANNAKER (University of

Melbourne) is thanked for the atomic absorption, H_2O^+ and CO_2 determinations; The CO_2 determinations were confirmed by Mr. L. C. BLAKEMORE (Soil Bureau) using the Leco method. Mr. G. ATKINS assisted with the neutron activation analyses. Dr. P. J. POTTS and M. SARRE (Open University) carried out neutron activation analysis of rare earths in the Timor nodule. A. J. FLEET (Open University) gave permission to quote rare earth data from a second Timor nodules. This research was supported in part by an Australian Institute of Nuclear Science Engineering grant to R.R.K. Drs. J. L. BISCHOFF, J. H. CROCKET, and H. W. NESBITT are thanked for their useful comments on the manuscript.

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