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Geochemistry of Oceanic Ferromanganese Deposits [and Discussion]

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Geochemistry of oceanic ferromanganese deposits

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[Plate 1]

Deposits of mixed manganese and iron oxides, with high concentrations of minor metals, cover large areas of the deep-sea floor. They occur as *nodules*, over a very wide depth range, but most abundantly on the abyssal sea floor in water depths between 4 and 5 km, and as *unconsolidated sediments*, *rocks* and *crusts*, which are restricted to areas of the world-wide active ridge system. The two types of deposit have different chemical compositions and are the products of different precipitation and accretion mechanisms on the abyssal sea floor.

Ferromanganese nodules grow very slowly, they generally have Mn/Fe ratios greater than or equal to 1, and they contain high levels of Ni, Cu, Co, Ba, Pb, Zn and Mo. Regional, inter- and intra-ocean variations in composition are marked. Such variations can be easily mapped throughout the Pacific and are most plausibly explained by a combination of the variety of metal sources on the sea floor (including abyssal water, biological debris and perhaps volcanism), and by the different environmental conditions under which the nodules form. Some of the variability in the contents of Ni and Cu, two of the metals for which the nodules are considered a valuable resource, can be interpreted as a reflection of intensive metal recycling and diagenetic reaction at the sediment surface.

Iron- and manganese-rich sediments, rocks and crusts accumulate quite rapidly, they have highly variable Mn/Fe ratios, and they contain a different suite of minor metals, generally at lower concentrations, compared with ferromanganese nodules. Compositional variations in this case are on the scale of an individual specimen as well as regional, although clear trends are not evident at the present time. They are thought to form by precipitation from the reaction products of newly extruded basalt and seawater; isotopic evidence also indicates that there is significant adsorption of metals from seawater by the poorly crystalline oxides produced by this reaction.

1. INTRODUCTION

The ferromanganese deposits in the deep sea represent an important class of authigenic mineral deposits forming at the present time. They result from diverse chemical reactions on the sea floor and can in principle be used to provide information on physical, chemical and biological processes taking place in the ocean as a whole. Significant advances have recently been made in providing information on their geochemistry, an essential prerequisite for understanding their wide compositional variations, their modes of formation and the distribution of particular deposits of potential ore grade.

There are essentially two types of marine ferromanganese deposits, representing two different modes of accumulation of iron and manganese. The well-known *ferromanganese nodules* are widely distributed over extensive areas of sea floor, as well as in many shallow-water environments and in lakes. They have been studied extensively since their discovery during the *Challenger* expedition (Murray & Renard 1891) and recent reviews of various aspects of their distribution and composition have been provided by Skornyakova & Andrushchenko (1972), Cronan (1974, 1976*a*), Margolis & Burns (1976) and Glasby (1977). Ferromanganese deposits of quite different character are found sporadically on or close to the mid-ocean ridge system. They occur as unconsolidated *sediments*, and as *crusts and rocks* of highly variable morphology and composition. Their discovery is more recent, and they are attracting a great deal of attention. Bonatti (1975) provides a useful review of their main features.

I shall discuss the geochemistries of the two classes of ferromanganese deposits in separate sections, stressing the more recent data available at the time of writing, before attempting to compare and contrast their compositions and modes of formation. I shall not include discussion of the metalliferous sediments of the hot brine deeps of the Red Sea (Degens & Ross 1969) because of their unique compositions and modes of formation (Manheim 1974), requiring a separate treatment.

2. FERROMANGANESE NODULES

2.1. *General*

Ferromanganese nodules are generally spheroidal or discoidal concretions, most commonly a few centimetres in diameter, which are most abundant on the surfaces of unconsolidated sediments in abyssal water depths (4–5 km). Estimates of the surface concentration of nodules in the Pacific, from sampling and from sea floor photographs (figures 1 and 2, plate 1), yield mean values of 10 kg m^{-2}, but reaching 38 kg m^{-2} (Mero 1965). Nodules also occur sporadically within the sediments (Cronan & Tooms 1967). Ferromanganese crusts on exposed rock surfaces have compositions broadly similar to the concretionary forms and are conveniently included in the discussion of nodule geochemistry.

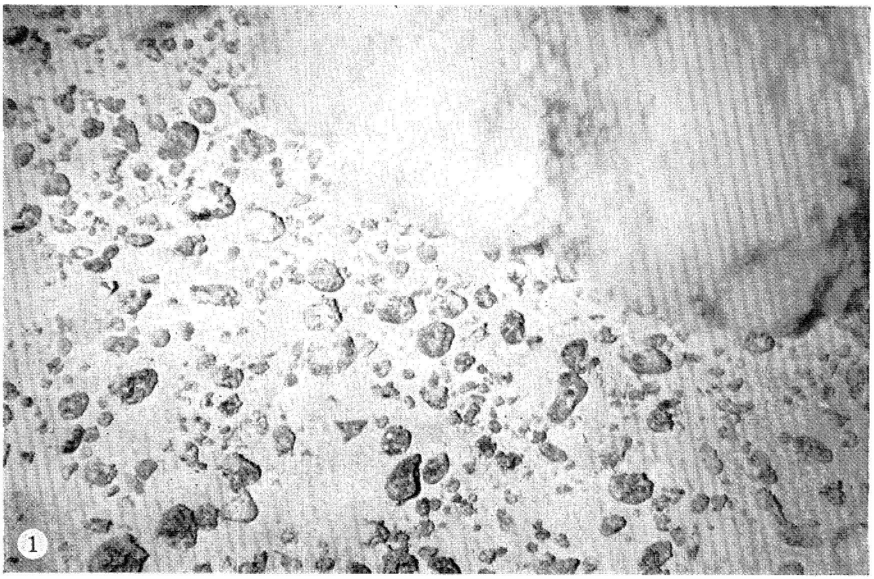
Ferromanganese nodules may or may not possess a central nucleus or core, consisting of rock or mineral fragments in various stages of alteration, skeletal material (carbonate tests, teeth or bones), fragments of older nodules, or pieces of sediment. The coating of ferromanganese and other materials is most commonly concentrically arranged around the nucleus, some individual layers and laminae being traceable around the entire circumference of the concretion (Sorem 1967; Sorem & Foster 1972). Individual shapes of nodules are often governed by the shapes of the nuclei.

2.2. *Chemical composition*

Ferromanganese nodules are composed of an intimate mixture of crystalline and amorphous phases. This includes oxyhydroxides of iron and manganese (see §2.3), detrital aluminosilicates, organic debris, mainly skeletal, and minor quantities of authigenic silicates, sulphates, etc. They are highly porous and contain a large proportion of bound water. The heterogeneous nature of the nodules must be borne in mind in any discussion of their bulk chemical composition.

Although the chemical compositions of sea-floor nodules from all major ocean basins have been reported, attention will be restricted here to the Pacific, where the data are most abundant. Mero (1965) and Cronan (1974, 1976*a*) have provided average composition for a few elements based on a large number of analyses. In view of the extreme compositional variability in the Pacific (see §2.5) and because most of the data consist of partial chemical analyses, selected individual analyses are shown in table 1, together with data on nearshore nodules and pelagic sediments.

Inspection of table 1 shows that Pacific nodules have Mn/Fe ratios close to or greater than 1 and detrital aluminosilicate contents, based on the Si and Al concentrations (Calvert & Price 1977*a*), of roughly 25 % by mass. Some significant fraction of the Fe, but not the Mn, in nodules



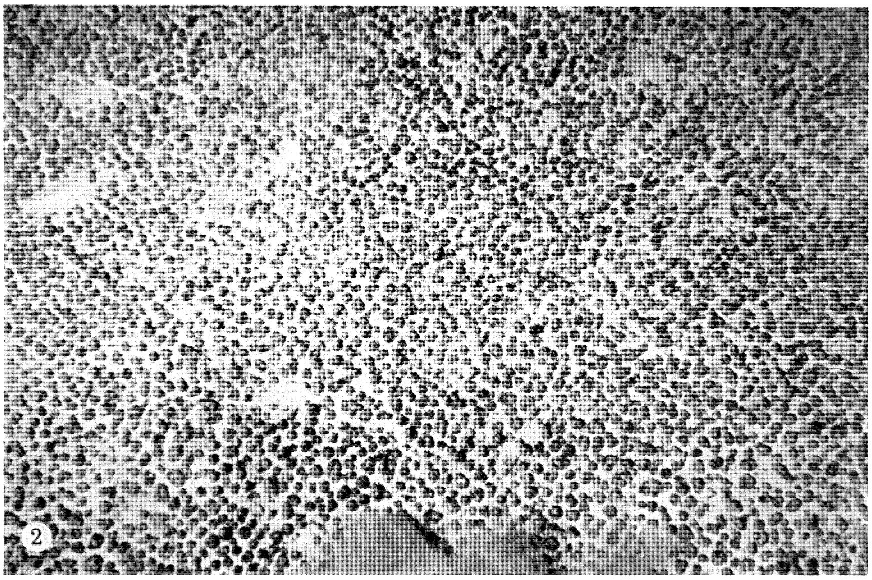


FIGURE 1. Sea-floor photograph at 20° 38′ N, 130° 46′ W, depth 5180 m. Nodules are 1–10 cm in diameter and irregular and discoidal in shape; many are partially buried in the fine clay substrate. Sediment cloud was caused by the camera touching the seabed. (U.S. Navy Photo.)

FIGURE 2. Sea-floor photograph at 13° 53′ S, 150° 35′ W, depth 3695 m. Nodules are 2–5 cm in diameter and are more or less spherical. The pale-coloured patches are mounds of sediment (calcareous ooze), probably thrown up by benthonic organisms, which cover the nodules. (U.S. Navy Photo.) The distance from the camera to the sea floor is larger in the bottom photograph.

is present in the aluminosilicate component so that the Mn/Fe ratio in the oxide fraction is higher than that shown by the data in table 1.

Of the remaining major elements listed in table 1, it seems clear that Ca, K, Mg, P and Ti are also present to some extent in the oxide fractions of the nodules. Calvert & Price (1977*a*) have shown that Ca, P and Ti contents are significantly correlated with the total Fe content, whereas Mg is related to the Mn content; K is probably located in the Mn-bearing phase.

Table 1. Representative chemical compositions of Pacific ferromanganese nodules, shallow water nodules and pelagic sediments

(Major elements in percentages by mass; minor elements in parts/10^6.)

	nodules						sediments		
element	1	2	3	4	5	6	7	8	9
Si	12.80	5.40	5.90	4.95	13.64	6.32	25.80	22.00	1.10
Al	2.60	2.00	2.40	1.80	4.35	2.27	9.20	6.50	0.40
Ti	0.62	0.56	1.27	0.89	0.08	0.21	0.65	0.38	0.12
Fe	11.40	6.40	16.40	14.05	1.36	3.92	5.60	4.50	0.80
Ca	1.60	1.60	2.20	6.85	0.87	5.56	0.70	1.60	32.10
Mg	0.90	1.70	1.40	—	—	1.87	2.00	2.00	1.70
K	0.80	1.00	0.75	0.39	1.52	1.03	2.85	2.07	0.05
P	0.15	0.19	0.33	0.08	—	0.35	0.08	0.40	0.22
Mn	13.20	24.90	16.00	14.4	24.8	30.20	0.80	0.91	0.60
CO_2	0.04	0.04	0.37	—	—	11.88	0.92	0.92	38.42
As	100	65	190	—	—	245	30	30	10
Ba	730	2 420	1 280	4 300	3 300	3 090	690	5 640	600
Co	2 000	2 400	4 400	7 000	170	120	190	280	290
Cu	2 300	10 100	900	720	460	17	300	700	200
Mo	250	610	375	430	320	55	40	40	15
Ni	4 600	12 500	2 000	2 900	1200	77	260	400	80
Pb	1 080	560	1 150	2 000	460	42	90	45	100
Rb	25	15	7	—	—	40	205	90	5
Sr	630	530	820	1 400	390	770	170	320	1 190
Y	95	130	160	—	—	28	50	290	30
Zn	600	860	390	400	430	60	200	270	110
Zr	360	290	380	—	—	55	190	200	30

Sources: 1, Station JYN II 8G, 40° 29′ N, 172° 32′ E, 4250 m depth (Calvert & Price 1977*a*, Table I). 2, Station JYN V 47PG, 14° 37′ N, 135° 04′ W, 4813 m depth (Calvert & Price 1977*a*, Table I). 3, Station AMPH 85PG, 11° 35′ S, 158° 31′ W, 5338 m depth (Calvert & Price 1977*a*, Table I). 4, Station MP 33K, 17° 48′ N, 174° 22′ W, 1810–2290 m depth (Mero 1965, Table XXX). 5, Station VS BII-35, 22° 18′ N, 107° 48′ W, 3000 m depth (Mero 1965, Table XXX). 6, Loch Fyne, Argyllshire, 200 m depth (Calvert & Price 1970, Table 2). 7, Pelagic clay, Station JYN VI 11G, 27° 42′ N, 175° 10′ E, 5750 m depth (Calvert & Price 1977*a*, Table I). 8, Siliceous clay, Station JYN V 43PG, 9° 53′ N, 138° 56′ W, 4893 m depth (Calvert & Price 1977*a*, Table I). 9, Calcareous ooze, Station AMPH 80G, 11° 51′ S, 160° 51′ W, 3803 m depth (Calvert & Price 1977*a*, Table I).

The data in table 1 also serve to illustrate the large degrees of enrichment of a wide range of elements in ferromanganese nodules compared with pelagic sediments. The nodules display extreme fractionations for the first and second row transition metals and As, Ba, Sr and Pb, as indeed do red clays relative to nearshore sediments (Wedepohl 1960).

There is a large degree of variability in the chemical composition of Pacific nodules, first described by Mero (1962). Abyssal sea-floor nodules from the north and south central Pacific have similar compositions, while those in the northern tropical area are enriched in Mn, Ba, Mo, Ni and Zn (table 1). Nodules collected on central oceanic seamounts have roughly equal Mn and Fe contents and are enriched in Co and Pb. Nodules from the eastern marginal areas have very high Mn/Fe ratios and relatively low minor element contents, these features resembling nodules from some shallow-water areas of rapid sedimentation (Calvert & Price 1977*b*).

The relations between some of the minor transition metals and Mn and Fe in ferromanganese nodules have been examined using bulk chemical (Goldberg 1954; Riley & Sinhaseni 1958; Mero 1962; Willis & Ahrens 1962; Ahrens *et al.* 1967; Cronan & Tooms 1969; Margolis & Burns 1976; Glasby *et al.* 1974; Glasby 1976; Calvert & Price 1977*a*) and electron microprobe (Burns & Fuerstenau 1966; Cronan & Tooms 1968; Friedrich *et al.* 1969; Dunham & Glasby 1974; Ostwald & Frazer 1973; Lalou *et al.* 1973*a*; Burns & Brown 1972) analyses. Significant positive correlations have been observed by various authors between Ni, Cu, Zn, Mo, Ba, Mg, K and Mn and between Co, Pb, Ti, V, Mo, Ce, Zr and Fe. Burns & Fuerstenau (1966) proposed that simple substitution of cations into the Mn- and Fe-bearing phases (see §2.3) could explain the observed correlations and this has been broadly confirmed by later work. The importance of a knowledge of the mineralogy of the various oxyhydroxide phases thus becomes apparent.

The relation between Co and the major Mn and Fe phases does not appear to be simple, however. Burns (1965) and Burns & Fuerstenau (1966) suggested that CoIII replaces FeIII in the iron oxyhydroxide phase in nodules and many bulk analyses of nodules show positive Co–Fe correlations. However, in some cases this relation is not observed, especially in abyssal nodules (Cronan & Tooms 1968; Ostwald & Frazer 1973). In addition, Price & Calvert (1970) pointed out that in seamount nodules the Co contents vary over very wide limits and do not appear to be related to the Fe content. For this reason, they suggested that CoIII (Goldberg 1961; Sillén 1961) enters into the highly oxidized δ-MnO_2 phase as well as into the Fe oxyhydroxide phase. Burns (1976) has provided a plausible mechanism for this process, involving the substitution of low-spin CoIII for MnIV in the structure and van der Weijden (1976) has presented evidence for the presence of Co in both the Mn and the Fe phases in a suite of Pacific Ocean nodules from a range of environments.

A further instructive example of fractionation exhibited by ferromanganese nodules concerns the distribution of the lanthanides. Oceanic nodules commonly display a marked Ce enrichment and variable enrichments of the other elements, relative to shales, depending on water depth. Nodules shallower than 3–3.5 km depth are enriched in Yb and Lu relative to Sm, Eu and Tb, whereas deeper nodules show marked depletions in Yb and Lu (figure 3). The shallow nodules have lanthanide patterns (apart from Ce) resembling that of seawater (Høgdahl *et al.* 1968) which is used as evidence for the derivation of these elements in nodules from seawater by coprecipitation (Goldberg *et al.* 1963). By contrast, the lanthanide patterns for the deeper nodules appear to be the mirror image of that of seawater (Piper 1974*a*).

Note that unlike the remaining lanthanides, Ce can exist in the CeIII and CeIV oxidation states in nature (Goldberg 1961). This could be the explanation of the extreme Ce enrichment in the highly oxidized nodules and the extreme Ce depletion in seawater relative to river water. In addition, seamount nodules, containing the more oxidized Mn phase (§2.3.1), have the most marked Ce anomaly (Piper 1974*a*), and indeed the highest concentrations of Co, Pb and Ti, metals which can also be oxidized in the marine environment (Sillén 1961; Price & Calvert 1970).

The depth at which the change in lanthanide patterns of ferromanganese nodules occurs in the Pacific (Piper 1974*a*) is close to the depth of the lysocline (Berger 1970), approximately 3.7 km where the solution rate of $CaCO_3$ shows a marked increase (Peterson 1966). Release of the lanthanide elements from dissolving biogenous tests and their coprecipitation with accreting ferromanganese oxyhydroxides could therefore explain the interesting contrast between deep and shallow-water nodules since Piper (1974*a*) has shown that foraminiferal tests, like the nodules, have Yb and Lu depletions relative to Sm and Eu.

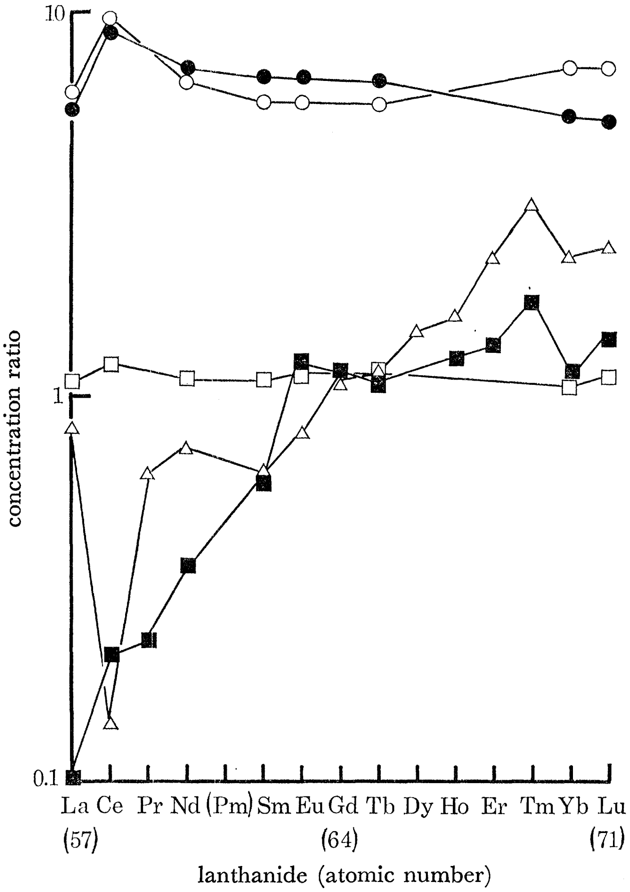


FIGURE 3. Distribution of the lanthanides in ferromanganese nodules and pelagic clay (from Piper 1974*a*), seawater (from Høgdahl *et al.* 1968) and Mid-Atlantic Ridge basalt (from Frey & Haskin 1964); ●, nodules from below 3000 m; ○, nodules from above 3000 m; □, pelagic clay; △, seawater ($10^7\times$ concentrations); ■, M.A.R. basalt. Concentration ratio is the ratio of each individual lanthanide to its concentration in average shale (Piper 1974*a*).

2.3. *Minerology*

Although the mineralogy of the manganese and iron oxyhydroxides in oceanic nodules has been difficult to elucidate, because of the very small sizes of the crystallites, the intimate intergrowth of authigenic phases and the presence of amorphous material, it seems clear from the available structural information that a great deal of the chemical variability of the nodules is due to a variable Mn phase mineralogy. There has been considerable confusion over nomenclature in the literature and this has recently been reviewed by Burns & Burns (1977).

2.3.1. *Manganese phases*

Using X-ray diffraction techniques, Buser & Grütter (1956) identified two different crystalline Mn phases in a small sample of oceanic ferromanganese nodules. They were referred to as δ-MnO_2, described as an essentially disordered two-dimensional layer structure characterized by reflexions at *ca.* 245 and 140 pm, and a double-layered structure, similar to that of lithophorite, consisting of MnO_2 sheets alternating with disordered layers containing Mn^{2+} and OH^- ions and H_2O. The structure of this latter phase was stated to be reasonably similar to that of the manganite group with the general formula $3MnO_2 . Mn(OH)_2 . xH_2O$ (Buser *et al.* 1954) having a characteristic basal reflexion at around 1000 pm. Grütter & Buser (1957) examined some other nodule samples and, in addition to the two phases already noted, identified a separate manganite phase, characterized by a reflexion at 710 pm. This phase is considered to be a more ordered form of δ-MnO_2, containing a higher proportion of MnII ions (Buser *et al.* 1954). Buser (1959) provided a summary of this work and listed the Mn phases in nodules as 10 Å manganite,† 7 Å manganite and δ-MnO_2 by comparison with synthetic preparations. The phases differ in oxidation grade and in specific surface area (Buser & Graf 1955), δ-MnO_2 being significantly finer-grained and more highly oxidized than 7 Å manganite.

TABLE 2. MANGANESE OXIDE MINERALS IN FERROMANGANESE NODULES (AFTER BURNS & BURNS 1977)

mineral	formula	crystal class	structure
todorokite	(Na, Ca, K, Ba, Mn^{2+}) $Mn_5O_{12} . 3H_2O$	monoclinic	unknown, but may be related to hollandite and psilomelane
birnessite	$4MnO_2 . Mn(OH)_2 . 2H_2O$ or (Ca, Na)(Mn^{2+}, Mn^{4+})$_7O_{14} . 3H_2O$	hexagonal	unknown, but may be related to chalcophanite
δ-MnO_2		hexagonal	possibly disordered, fine-grained birnessite

Subsequent work (see Manheim 1965) has shown that naturally occurring todorokite (Yoshimura 1934) is similar to 10 Å manganite and that birnessite (Jones & Milne 1956) has an identical X-ray diffraction pattern to that of 7 Å manganite. On the basis of the occurrence of these natural phases and their identification in ferromanganese nodules, Burns & Burns (1977) recommended the adoption of the nomenclatural scheme outlined in table 2. Note that Burns & Brown (1972) previously suggested that the X-ray reflexion at around 710 pm was a 101 plane of the 10 Å manganite rather than a discrete phase, and the term birnessite has been used for both birnessite (*sensu* Jones & Milne 1956) and δ-MnO_2 (Glemser *et al.* 1961; Bricker 1965; Cronan & Tooms 1969), and that todorokite is considered to be a mixture of *buserite* and its alteration products by Giovanoli *et al.* (1973) and Giovanoli & Bürki (1975).

The identification of the Mn phases in ferromanganese nodules by conventional X-ray diffraction methods presents some problems. Reflexions at around 245 and 140 pm are common to all three phases listed in table 2: it is not therefore possible to detect δ-MnO_2 in the presence of either of the other phases from line spacings alone. Burns & Burns (1977) recommend using peak intensities at 960, 710 and 245 pm to detect δ-MnO_2 in the presence of todorokite or birnessite. Lyle *et al.* (1977) have used this approach in a study of nodules from the southeastern Pacific. A separate problem surrounds the identification of birnessite, since a reflexion due to phillipsite, a most common accessory mineral in Pacific ferromanganese nodules, is also found at around 710 pm and the reflexion at 360 pm in birnessite is weak (Jones & Milne 1956). Although this phase is not as widely distributed in nodules as the other two phases, it does seem likely that previous identifications could be in error due to this interference. Figure 4 shows X-ray diffraction patterns of two nodule samples illustrating the problem.

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† 1 Å = 10^{-10} m = 0.1 nm.

The regional distribution of the various Mn-bearing phases in nodules from the Pacific was first reported by Barnes (1967*a*). Glasby (1972*a*) has provided additional data, including that from Cronan (1967), and the combined information is shown in figure 5. It should be noted that only two phases are recognized here, namely todorokite and δ-MnO_2, because of the problems discussed above. Samples classified in the 7 Å manganite category by Barnes (1967*b*) are placed in the todorokite class, because they also contain todorokite and δ-MnO_2. It is apparent that todorokite occurs mainly in the eastern marginal Pacific and in two east-west zones in the northern and southern tropical areas. δ-MnO_2 occurs separately in the western Pacific. Although Barnes (1967*a*) also pointed out that δ-MnO_2 is the common phase in seamount nodules and suggested a hydrostatic pressure control on mineralogy, Glasby (1972*b*) has shown that the pressure range involved is too small to have an appreciable effect on the phases formed.

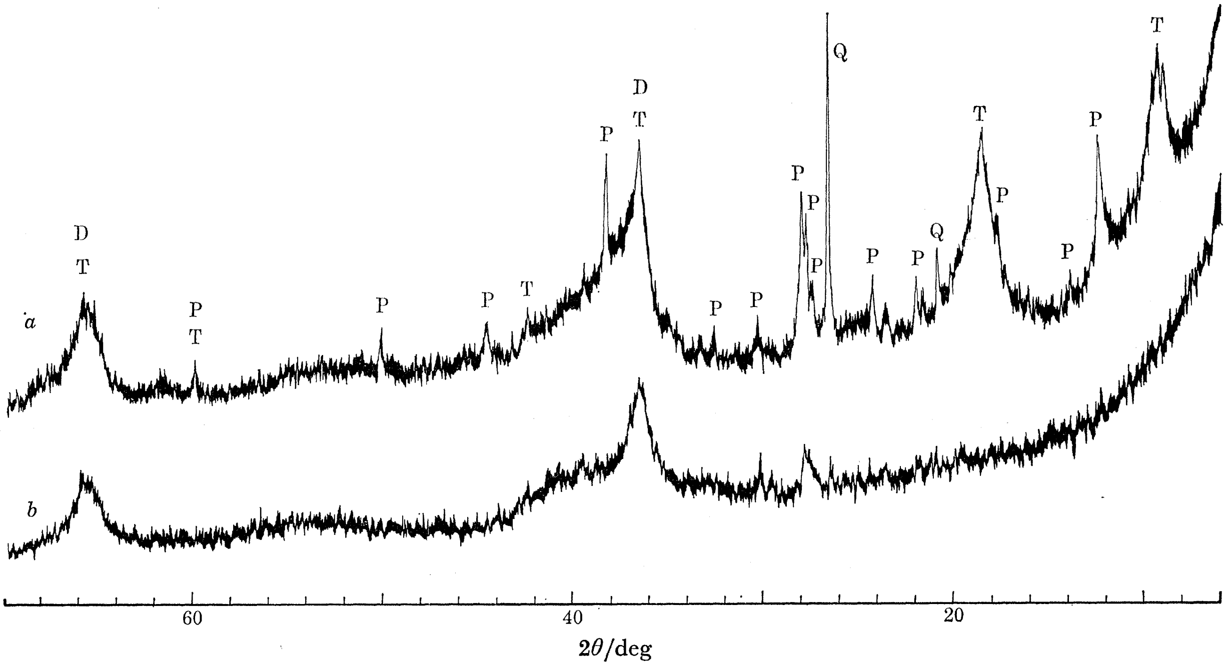

FIGURE 4. X-ray (CuKα) powder diffraction patterns of ferromanganese nodules from the Pacific Ocean. (*a*) Sample WAH 18F3, 8° 16′ N, 152° 58′ W, water depth 5133 m. Contains todorokite (T) and δ-MnO_2 (D), as well as phillipsite (P) and quartz (Q). Chemical composition given in Calvert *et al.* (1978). (*b*) Sample AMPH 80, 11° 51′ S, 160° 51′ W, water depth 3803 m. Contains δ-MnO_2 and minor amounts of phillipsite and quartz. Chemical composition given in Calvert & Price (1977*a*).

Moreover, Skornyakova *et al.* (1975) and Calvert & Price (1977*a*) showed that some abyssal sea floor nodules in the central and southwestern Pacific, occurring at abyssal depths, contained only δ-MnO_2. It seems reasonable to conclude, therefore, that the mineralogy is governed by the environment of nodule formation rather than water depth *per se* (Cronan & Tooms 1969; Price & Calvert 1970; Glasby 1972*a*).

The mineralogy of the Mn phase in nodules is an important determinant of their minor element composition (Barnes 1967*a*; Cronan & Tooms 1969). Thus, nodules containing todorokite appear to contain, for example, more Cu, Mo, Ni and Zn, and nodules containing only δ-MnO_2 have more Ce, Co, Pb and Ti, as discussed in §2.2. Although some of this variation may be produced by the very different environments represented by the abyssal seafloor and seamounts, where Co enrichment is particularly marked, figure 6 shows that the mineralogy significantly influences the Ni content of abyssal sea floor nodules. These observations suggest, therefore, that we would expect some regional variation in the minor element composition of nodules and that this would be basically like that shown in figure 5. This has been confirmed by Cronan & Tooms (1969), Calvert & Price (1977*a*) and Piper & Williamson (1977) and will be discussed in §2.5.

Figure 5. Distribution of todorokite and δ-MnO_2 in nodules from the Pacific Ocean. Data from Barnes (1967*b*) and Glasby (1972*a*). Samples labelled ● contain todorokite and δ-MnO_2; samples labelled △ contain only δ-MnO_2. Samples included in a '7Å manganite' category by Barnes (1967*a*, *b*) are designated todorokite in this figure, since they contain both todorokite and δ-MnO_2 and because of the possible interference by phillipsite in the identification of this phase.

2.3.2. *Iron phases*

The mineralogy of the iron-bearing phase or phases in ferromanganese nodules is much less well known. Buser & Grütter (1956) identified goethite (α-FeOOH) in hydroxylamine-insoluble residues from oceanic nodules. Geothite has been reported most commonly in shallow-water nodules (Manheim 1965; Calvert & Price 1977*b*), whereas later reports on oceanic nodules have described the iron phase as amorphous (Goodell *et al.* 1971; Glasby 1972*c*). It is possible that the Fe is present as a hydrated ferric oxide polymer (Towe & Bradley 1967) which may be identical to a natural ferric gel (Coey & Readman 1973) and the mineral ferrihydrite, $2.5\ Fe_2O_3 . 4.5\ H_2O$ (Chukrov *et al.* 1973), possessing very short-range order and consequently being virtually amorphous to X-rays (Giovanoli & Bürki 1975; Burns & Burns 1977).

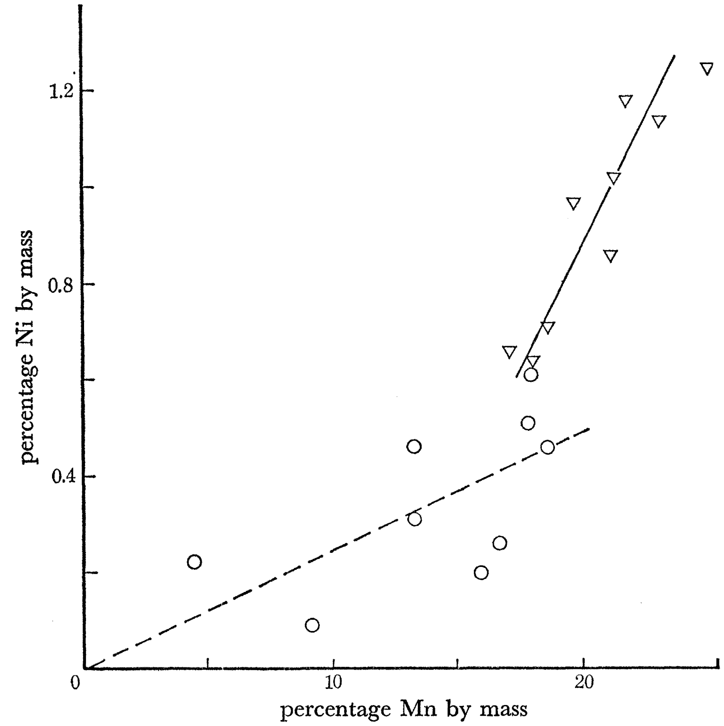

FIGURE 6. Relation between the Mn and Ni contents of ferromanganese nodules from the abyssal Pacific, illustrating the mineralogical control on minor metal concentrations (from Calvert & Price 1977*a*): ▽, todorokite; ○, δ-MnO_2.

Burns & Burns (1975) have suggested that δ-MnO_2 and ferrihydrite (or Fe III oxide hydroxide) are probably isostructural and form epitaxial intergrowths in ferromanganese nodules. This association is considered to be responsible for the nucleation of oxyhydroxide precipitation and to inhibit the formation of more ordered structures in nodules. Burns & Burns (1975) have further argued that longer range ordering may proceed under high hydrostatic pressures to produce todorokite. This cannot be verified at present since it is well known that todorokite occurs in shallow-water nodules (see Calvert & Price 1977*b*) and that nodules containing only δ-MnO_2 and δ-MnO_2 together with todorokite occur at similar water depths in the equatorial Pacific (Calvert & Price 1977*a*). The important factor may be the abundance of iron in the nodules, which prevents ordering, since todorokite-free nodules have significantly lower Mn/Fe ratios than todorokite-bearing nodules. A similar relation between the mineralogy and the bulk composition of nodules has been noted by Lyle, Dymond & Heath (1977).

2.4. *Growth rates*

The rate of growth of ferromanganese nodules has been measured by a number of radiometric techniques, including ^{230}Th/^{232}Th, excess ^{230}Th, K/Ar, ^{10}Be, gross α-activity, and by hydration rind dating. Rates measured by ^{230}Th and ^{10}Be techniques (Bhat *et al.* 1973) and by ^{230}Th and hydration rind methods (Burnett & Morgenstein 1977) appear to be concordant.

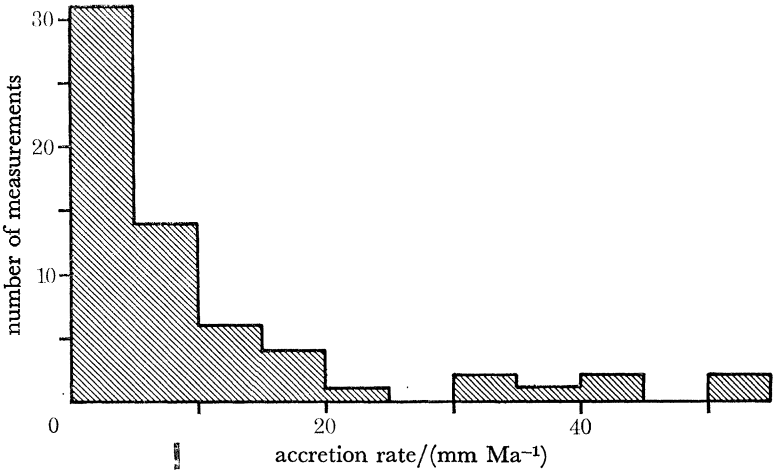

Figure 7. Measured growth rates of ferromanganese nodules. Data from Goldberg (1961), Nikolayev & Yefimova (1963), Bender *et al.* (1966, 1970), Somayajulu (1967), Barnes & Dymond (1967), Ku & Broecker (1969), Krishnaswami & Lal (1972), Bhat *et al.* (1973), Heye & Beiersdorf (1973), Kraemer & Schornick (1974) Boulad *et al.* (1975), Sugimura *et al.* (1975), Burnett & Morgenstein (1976) and Heye & Marchig (1977).

Figure 7 shows the frequency distribution of the available growth rate measurement on Pacific nodules. A median rate close to 5 mm Ma^{-1} appears reasonable. The difference between this rate and the rate of accumulation of Pacific pelagic sediments, of the order of 2 m Ma^{-1} (Ku *et al.* 1968), is well known and mechanisms for maintaining the slower growing nodules at the sediment surface have been extensively debated.

Lalou & Brichet (1972) and Lalou *et al.* (1973*b*) have argued that nodule growth rates are in fact much higher than are derived from radiometric measurements. They maintain that the ^{230}Th is deposited on the nodule surface after formation, the exponential decrease in activity of the isotope in the near-surface layers of a few millimetres thickness being an artefact of this process and not due to radioactive decay. Lalou *et al.* (1973*b*, *c*) further argue that a higher ^{230}Th activity and the presence of ^{14}C in a phosphatized limestone nucleus in a Pacific nodule is firm evidence for rapid growth, although this is contested by Bouland *et al.* (1975).

The suggestion that nodules grow episodically, periods of rapid growth alternating with periods of dormancy, is also made by Lalou & Brichet (1972) and Lalou *et al.* (1973*a*) and explains some of the features of the microlaminated structure of nodules (Sorem & Foster 1972; Margolis & Glasby 1973). This is supported by some recent gross α-activity measurements on Pacific nodules by Heye (1975) who has found that exceptionally Mn-rich zones have growth rates in excess of 50 mm Ma^{-1} whereas Fe-rich zones represent periods of extremely slow growth. Average accretion rates from 24 individual nodules were in the range 4–9 mm

Ma^{-1} (figure 7). He also noted that buried nodules show no recent growth by the radiometric method used.

There appears to be a relation between nodule growth rates and their compositions (Piper & Williamson 1977; Heye & Marching 1977), Mn-rich nodules growing significantly more rapidly (figure 8). This may be due to the different modes of formation of nodules with different compositions, as discussed in §4.

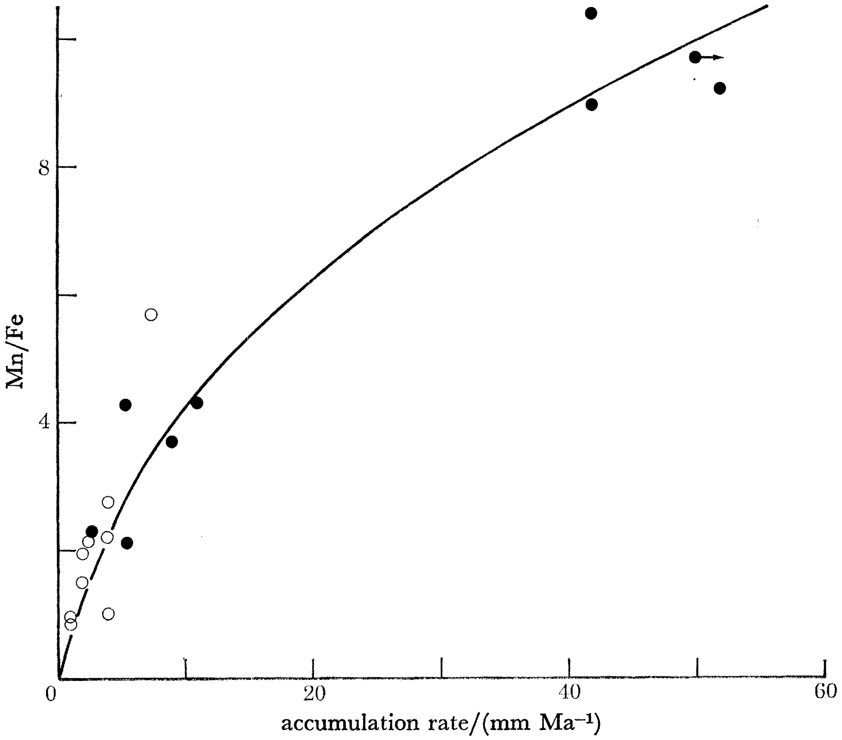

FIGURE 8. Relation between the composition, as expressed by the Mn/Fe ratio, and the growth rate of ferromanganese nodules. Data from Krishnaswami & Lal (1972) (○) and Heye & Marchig (1977) (●).

2.5. *Regional variations in composition*

The chemical composition of ferromanganese nodules appears to vary from ocean to ocean (Mero 1965), and significant differences are found between nodules from different topographic or sedimentary provinces (§2.2). In addition, Mero (1962) discovered profound variations in the composition of nodules throughout the Pacific Ocean. Later work (Mero 1975; Cronan & Tooms 1969; Price & Calvert 1970; Calvert & Price 1977*a*; Piper & Williamson 1977) has confirmed this regional variation, which has entered into some of the recent discussions of the mode of formation of the nodules.

Mero (1962) pointed out that crude compositional regions could be recognized in the Pacific, different areas being characterized by Mn-rich, Cu- and Ni-rich, Fe-rich, and Co- and Pb-rich nodules. Price & Calvert (1970) considered a larger number of analyses of abyssal seafloor nodules and examined compositional differences throughout the Pacific by using element ratios, thereby removing the effects of diluent aluminosilicate material. They showed that the Mn/Fe ratio varied remarkably smoothly throughout the basin, high ratios occurring in the eastern marginal areas, and in an east–west belt centred at about 10° N, and low ratios occurring in the northwestern and southwestern areas. Figure 9 shows the distribution of this

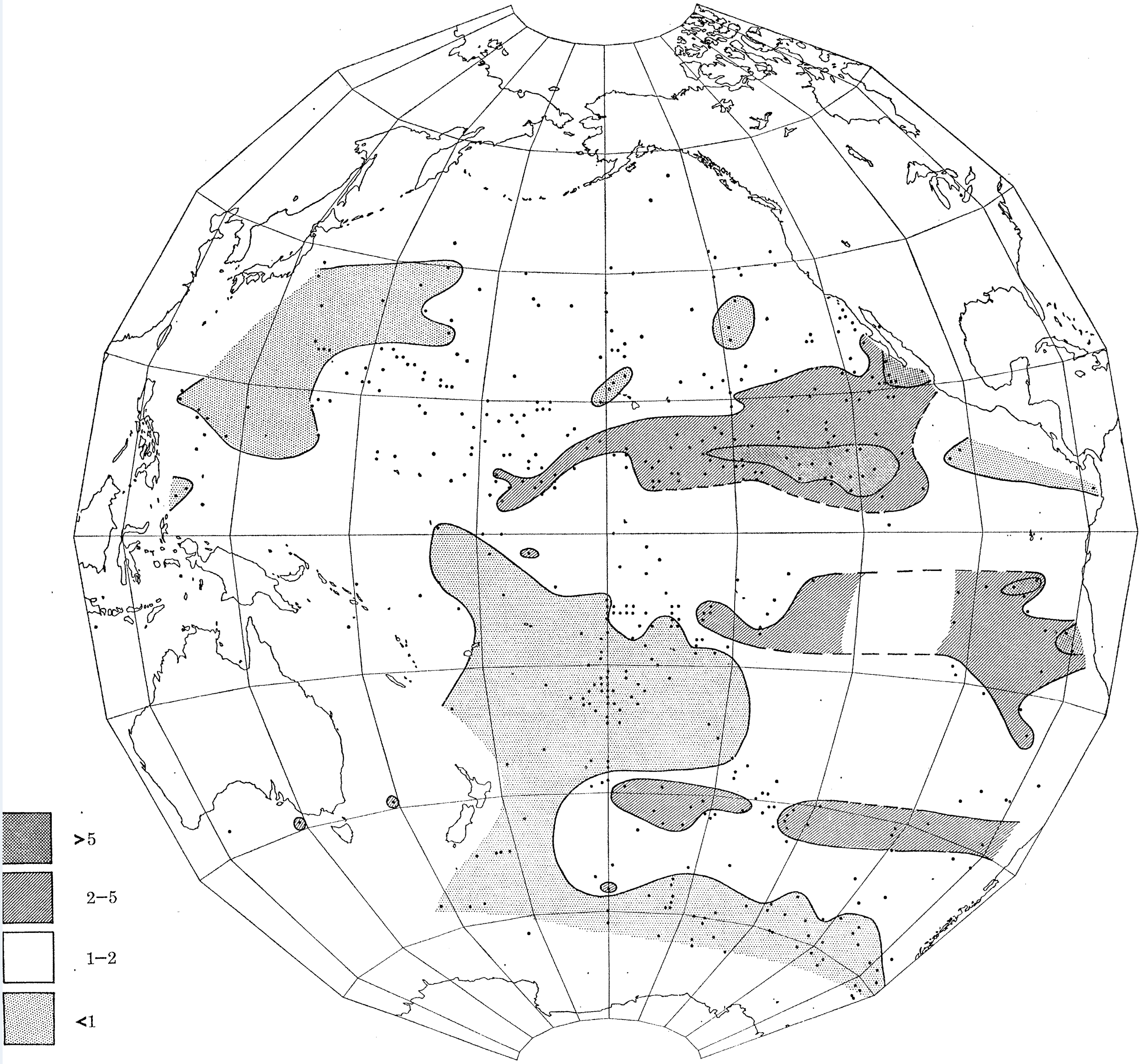

FIGURE 9. Distribution of Mn/Fe ratios in ferromanganese nodules from the Pacific. Data from Willis (1970), Horn *et al.* (1973), Glasby *et al.* (1975), Meylan & Goodell (1976), Skornyakova (1976) and Calvert & Price (1977*a*).

ratio using more extensive data; the trends are very similar to those reported by Piper & Williamson (1977). Apart from the eastern marginal areas, high ratios are found in three east–west belts centred at approximately 10° N, 10° S and 40° S, while lowest ratios (below 1) are found in the northwestern and southwestern areas.

Regional variability is also evident in the concentration of some of the minor elements in ferromanganese nodules. Figure 10 shows that Ni is enriched in the abyssal areas where nodules are enriched in Mn and figure 11 shows that Co is enriched in the areas where the nodules have lower Mn contents relative to Fe. This is where the large seamount and atoll chains are found and reflects the enrichment of Co in nodules from this environment, as discussed in §2.2.

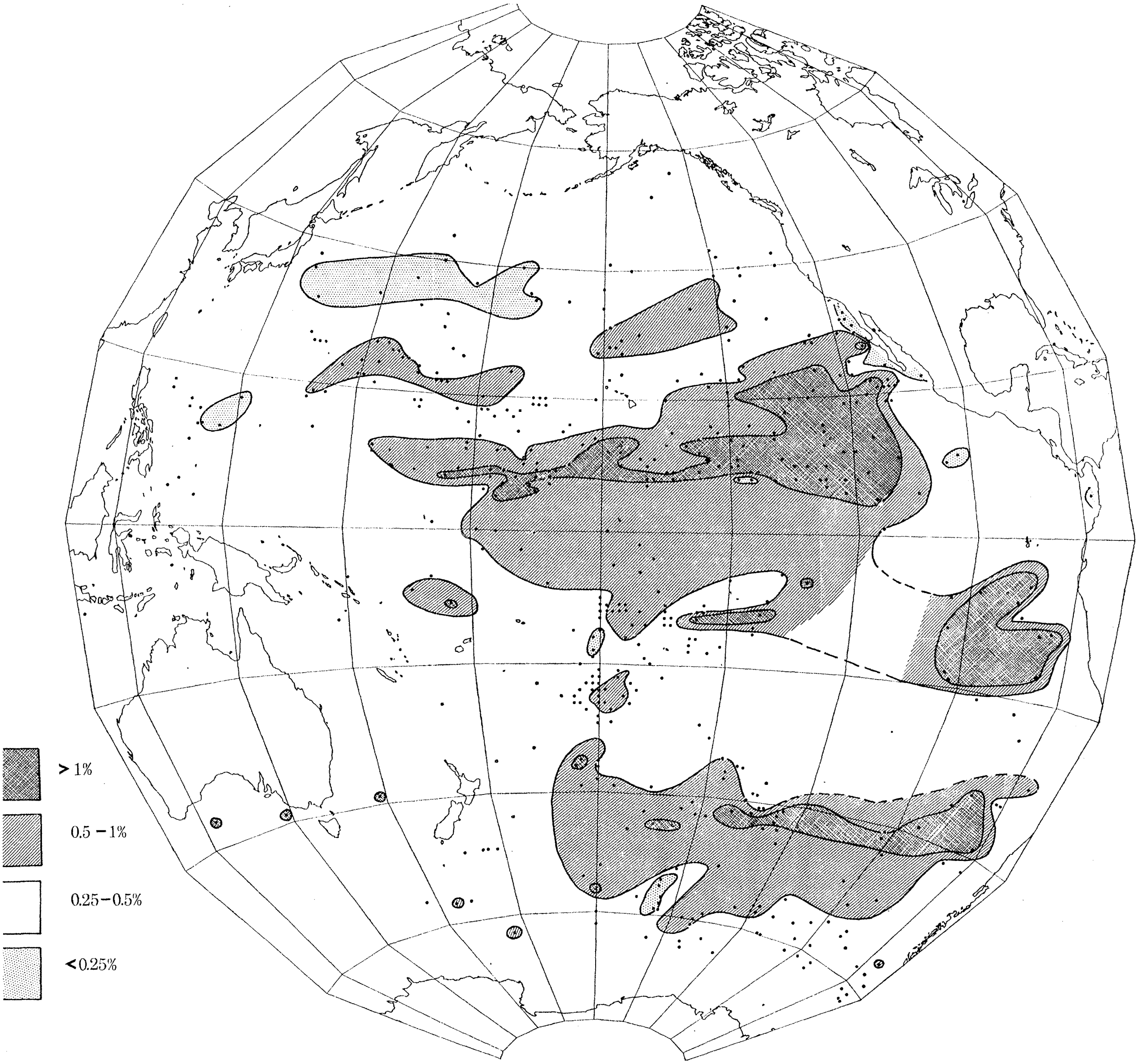

Figure 10. Distribution of nickel concentrations in ferromanganese nodules from the Pacific Ocean. Data sources as in figure 8. Copper shows a very similar distribution.

Using bulk chemical analyses, Calvert & Price (1977*a*) showed that the concentrations of a large group of major and minor elements, in addition to those shown in figures 10 and 11, also vary regionally in the Pacific since they are associated with either the Mn or the Fe phases of the nodules. Thus, Ba, Cu, Mo and Zn are related to the Mn contents and are highest in the northern equatorial region, whereas As, Ce, Pb, Sr, Y, Zr, Ti and P are related to the Fe contents and are highest where Mn/Fe ratios are lowest. These two groups of nodules also have different mineralogies (see figure 5). The Mn-rich nodules contain todorokite and δ-MnO_2, whereas the Fe-rich nodules contain only δ-MnO_2, the latter occurring on seamounts and on the abyssal sea floor.

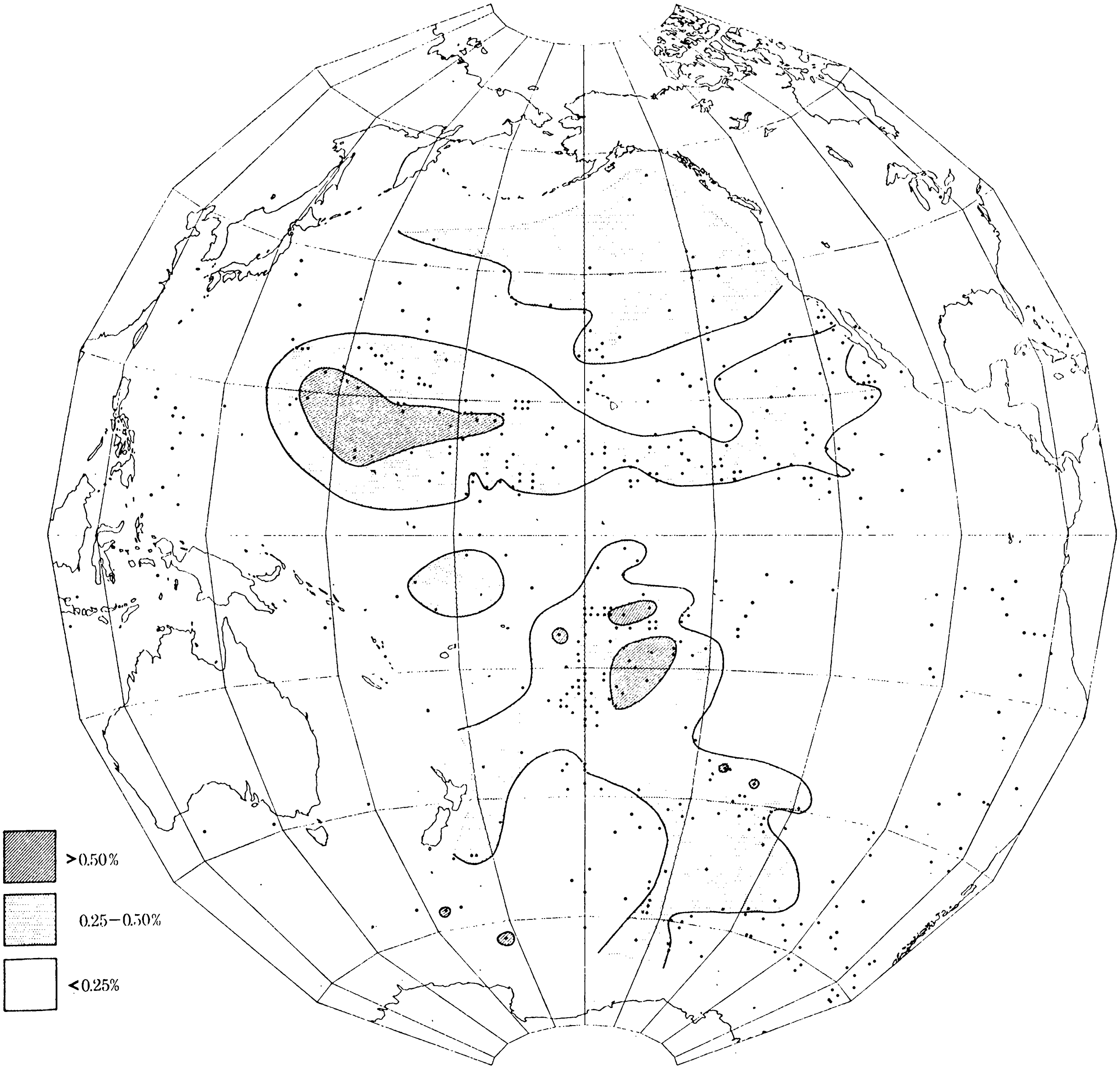

Figure 11. Distribution of cobalt concentrations in ferromanganese nodules from the Pacific Ocean. Data sources as in figure 8.

3. RIDGE CREST FERROMANGANESE DEPOSITS

3.1. *General*

Ferromanganese deposits of very variable form and composition are found sporadically on, or are associated with, the mid-ocean ridge system (figure 12). Revelle (1944) showed that the unconsolidated sediments in the southeastern Pacific contained high concentrations of Mn (see also El Wakeel & Riley 1961), and Skornyakova (1964) identified the East Pacific Rise (E.P.R.) area as a site of dispersed Mn and Fe enrichment. Subsequently, Boström & Peterson (1966) described the metal content of the E.P.R. sediments in some detail and further studies of these unusual sediments have been reported by Boström *et al.* (1969), Boström (1970) Boström & Peterson (1970), Bender *et al.* (1971), Piper (1973), Dymond *et al.* (1973), Dymond & Veeh (1975) and Heath & Dymond (1977).

Ferromanganese sediments also occur to the east of the E.P.R. in an area known as the Bauer Deep (B.D.) (Revelle 1944). They have been described by Dasch *et al.* (1971), Bischoff & Sayles (1972), Sayles & Bischoff (1973), Sayles *et al.* (1975), Bagin *et al.* (1975) and Heath & Dymond (1977).

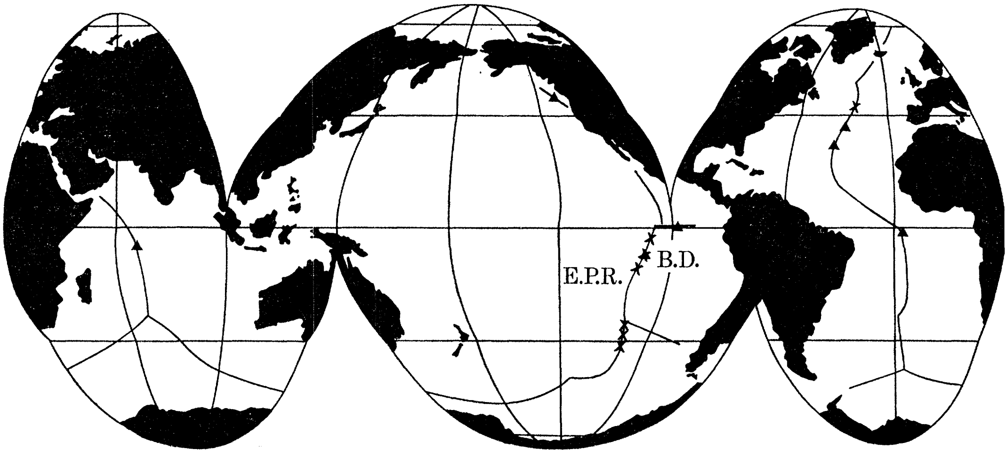

FIGURE 12. Occurrences of ferromanganese sediments, rocks and crusts on the mid-ocean ridge. E.P.R., East Pacific Rise; B.D., Bauer Deep; ▲, iron/manganese-rich crusts and crusts; ×, metalliferous sediment. Individual occurrences taken from Baturin (1971), Cronan (1972), M. R. Scott *et al.* (1974), Piper *et al.* (1975), Arcyana (1975), Bonatti *et al* (1976), Moore & Vogt (1976) and Burnett & Piper (1977).

As a result of deep drilling in the ocean basins (Joides 1967), ferromanganese-rich sediments are also known to occur above basaltic basement in many areas of the eastern Pacific (figure 13), as well as in the Atlantic and Indian Oceans. They are thought to have formed initially at active ridge crests and have since moved to their present positions as a result of sea-floor spreading. Their compositions have been reported by von der Borch & Rex (1970), von der Borch *et al.* (1971), Cook (1971), Drever (1971), Cronan *et al.* (1972), Cronan (1973, 1976*b*) and Cronan & Garrett (1973).

In addition to the unconsolidated ridge-crest sediments, ferromanganese crusts and rocks are also found on the mid-ocean ridge (figure 12). They represent isolated occurrences and have been recovered as a result of sporadic dredge sampling on topographic elevations or in fracture zones. More recently they have been systematically sampled from submersibles (Arcyana 1975).

3.2. *Chemical composition*

Representative analyses of ferromanganese deposits from ridge crest areas given in table 3 show that there is a much greater degree of variability in these deposits compared with ferromanganese nodules. The unconsolidated sediments have Mn/Fe ratios between 0.2 and 0.4 whereas the rocks and crusts have Mn/Fe ratios ranging from 0.002 to 39200. The aluminosilicate content of the deposits is quite low in the E.P.R. and basal metalliferous sediments and in the ironstones, whereas it is roughly the same as that in ferromanganese nodules in the B.D.

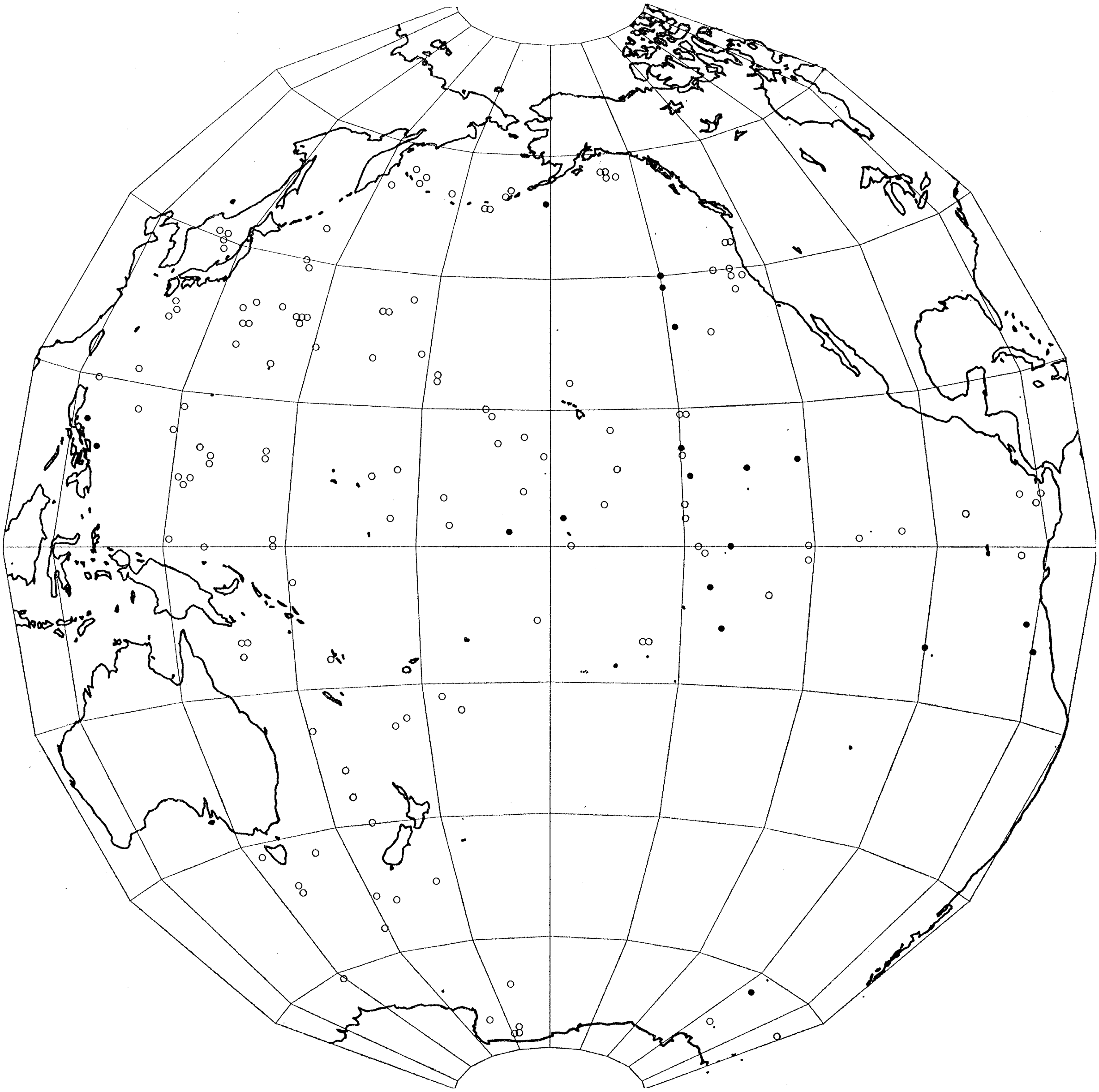

Figure 13. Distribution of basal metalliferous sediments in the Pacific Ocean. ○, D.S.D.P. drill sites; ●, metalliferous section present. Data taken from *Initial reports of the Deep Sea Drilling Project.*

sediments. Figure 14 shows that these deposits can be distinguished fairly easily from normal pelagic clays and from nodules.

Minor-element concentrations are also higher in the ridge-crest sediments compared with pelagic clays; in fact, As, Ba, Mo, Sr, Y, Zn and Zr contents are as high as those in nodules (table 3). Cobalt, Cu, Ni and Pb contents, on the other hand, are lower than those in nodules. Figure 15 shows that the deposits can also be distinguished from nodules on the basis of their Cu, Ni and Zn contents; nodules generally have Ni/Cu ratios greater than 1 whereas ridge crest sediments have Ni/Cu less than 1. Other elements enriched in ridge-crest sediments compared with pelagic clays include Ag, B, Cd, Hg, P, Tl and U (Boström & Peterson 1969; Boström & Fisher 1969; Fisher & Boström 1969; Horowitz 1970; Cronan 1972; Berner 1973).

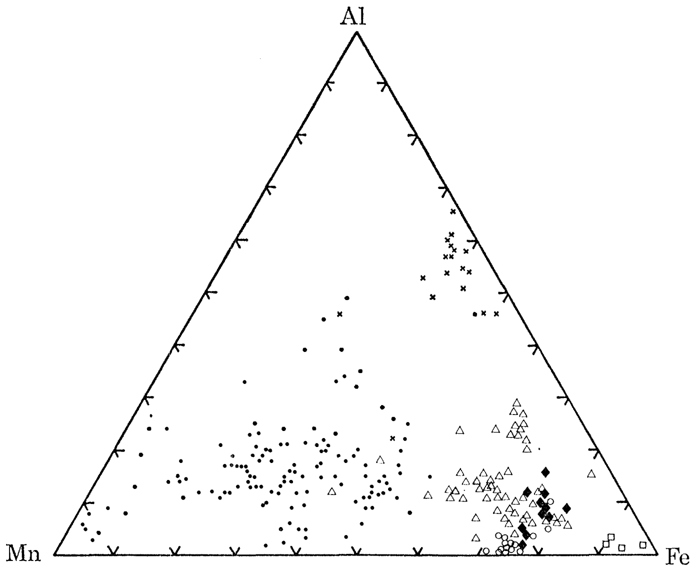

FIGURE 14. Composition of oceanic ferromanganese deposits on the basis of Mn–Fe–Al contents. Data sources: nodules (●), Mero (1965); E.P.R. (○) and B.D. (△) sediments, Heath & Dymond (1977); D.S.D.P. basal sediments (◆), S. E. Calvert, P. K. Studdart & K. Hampton (unpublished); ironstones (□), Bonatti & Joensuu (1966) and Piper *et al.* (1976); pelagic clays (×), Calvert & Price (1977*a*).

TABLE 3. CHEMICAL COMPOSITION OF METALLIFEROUS RIDGE-CREST SEDIMENTS, CRUSTS AND ROCKS

(Major elements in percentages by mass; minor elements in parts/10^6.)

element	1	2	3	4	5	6	7	8	9	10
Si	6.12	17.43	19.5	8.50	—	6.8	8.6	—	—	5.6
Al	0.51	3.24	2.61	2.75	—	0.5	1.0	—	—	0.8
Ti	—	—	—	0.25	—	—	—	—	—	0.07
Fe	30.20	15.83	13.6	23.14	0.06	30.8	28.5	0.22	21.8	39.0
Ca	—	—	1.74	1.67	—	1.8	1.3	—	—	0.14
Mg	—	—	2.39	1.52	—	0.6	0.7	—	—	0.24
K	—	—	0.85	1.25	—	0.3	0.3	—	—	0.25
Mn	9.92	5.74	3.83	4.77	39.0	1.65	2.05	54.6	16.7	0.08
P	—	—	—	0.60	—	—	—	—	—	—
As	—	—	—	250	—	—	—	—	—	—
Ba	6000	18600	18266	1633	—	105	267	—	—	80
Co	—	—	176	113	19	62	5	34	508	28
Cu	1450	1171	1084	1043	43	85	6	51	735	35
Mo	—	—	—	233	—	—	—	—	—	—
Ni	642	1066	1021	721	353	317	54	181	1950	170
Pb	—	—	—	112	—	—	—	—	—	—
Rb	—	—	—	53	—	—	—	—	—	—
Sr	—	—	1178	873	—	583	—	—	—	—
Y	—	—	—	120	—	—	—	—	—	< 5
Zn	594	413	376	667	—	—	450	2023	543	—
Zr	—	—	—	133	—	—	—	—	—	60

Sources: 1, East Pacific Rise sediment, mean of 7 samples on a carbonate-free basis (Heath & Dymond 1977, Table 2). 2, Bauer Deep sediment, mean of 7 samples on a carbonate-free basis (Heath & Dymond 1977, Table 2). 3, Bauer Deep sediment, mean of 56 samples on a carbonate-free basis (Sayles *et al.* 1975, Table 3). 4, Basal metalliferous sediments, mean of 9 samples, on a total sample basis, from D.S.D.P. Sites 37, 39 and 66, eastern Pacific (S. E. Calvert, P. K. Studdart & K. Hampton, unpublished data). 5, Manganese crust from Tag hydrothermal field 27° N Mid-Atlantic Ridge; mean of 7 samples (M. R. Scott *et al.* 1974, Table 2). 6, Ironstone from Station AMPH D2, 10° 38′ S, 109° 36′ W, 1790–2130 m depth, East Pacific Rise; mean of 3 samples (Bonatti & Joensuu 1966, Table 1). 7, Ironstone from Dellwood Seamount, Northeast Pacific; single sample (Piper *et al.* 1975, Table 1). 8, Manganese crust from Galapagos Spreading centre, 02° 42′ N, 95° 13′ W, 2562 m depth; mean of 7 samples (Moore & Vogt 1976, Table 1). 9, Ferromanganese crust from Galapagos Spreading Centre, 02° 17.8′ N, 101° 1.5′ W, 3150 m depth; single sample (Burnett & Piper 1977, Table 1). 10, Sulphide concretion from Romanche Fracture Zone, Mid-Atlantic Ridge; single sample (Bonatti *et al.* 1976, Table 1).

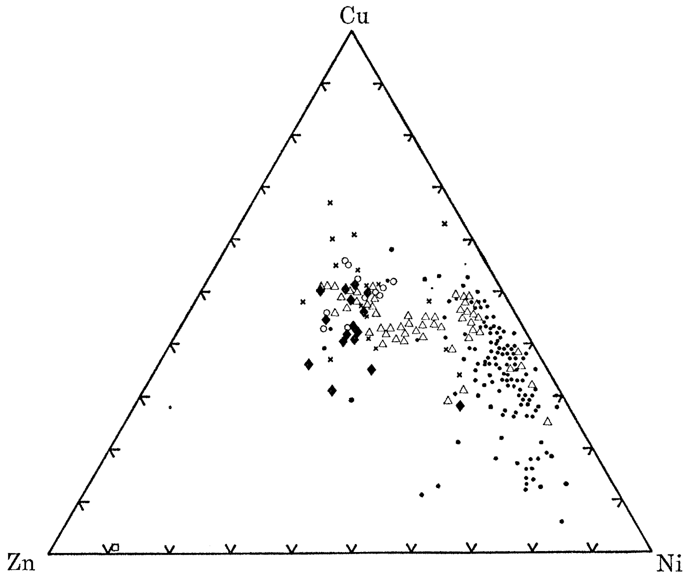

Figure 15. Composition of oceanic ferromanganese deposits on the basis of Cu–Ni–Zn contents. Data sources as in Fig. 13.

In contrast to the metal-enrichment in ridge-crest sediments, the rocks and crusts are markedly deficient in minor metals (table 3). The available data also suggest that Ni/Cu ratios are greater than unity.

The partition of some of the major and minor elements between different mineral phases (see §3.3) in the ridge-crest and basal metalliferous sediments has been examined using leaching procedures by Cronan & Garrett (1973), Sayles & Bischoff (1973), Sayles *et al.* (1975), Cronan (1976*b*) and Heath & Dymond (1977). In the E.P.R. sediments, Mn, Fe, Co, Ni, Cu and Zn are mainly present in oxyhydroxide phases whereas in the B.D. significantly more Fe is located in a smectite phase. In the basal metalliferous sediments, Cu and Zn appear to be mainly associated with goethite whereas a higher proportion of the Pb and almost all the Co and Ni are associated with Mn oxyhydroxides. Eklund (1974) has examined the composition of discrete todorokite, smectite and mixed oxide/silicate particles in B.D. sediments and has confirmed these patterns.

The distributions of the lanthanides in ridge-crest ferromanganese deposits show some distinct differences from those in ferromanganese nodules (§2.2). In the unconsolidated sediments, the absolute concentrations of the lanthanides are lower than in pelagic clays and the shale-normalized pattern is very similar to that of seawater (figure 16). This has been used as firm evidence for the derivation of the lanthanides from seawater without significant fractionation. However, Dymond *et al.* (1973) have suggested that the presence of significant amounts of phosphatic fish debris, which concentrates lanthanides from seawater (Arrhenius & Bonatti 1965), could affect the lanthanide patterns in such sediments, although Piper & Graef (1974) could not corroborate this. Eklund (1974) has shown that fish debris in Bauer Deep sediments contains less than 100 parts Ce/10^6 and 2400–3500 parts La/10^6 and, on the basis of the abundance of this material in these sediments, has suggested that the low Ce/La ratio in the bulk sediment may simply reflect mixing of components with different lanthanide contents.

The lanthanide patterns of ridge-crest ironstones and crusts appears to be highly variable (figure 16). A pattern similar to that of seawater has been obtained for the Mn-rich crust from the Galapagos Spreading Centre (Burnett & Piper 1977), whereas a pattern similar to that of basalt is obtained for the Dellwood Seamount ironstone (Piper *et al.* 1975). In the case of the Romanche Trench sulphide concretion, the pattern is quite unlike either of the other distributions.

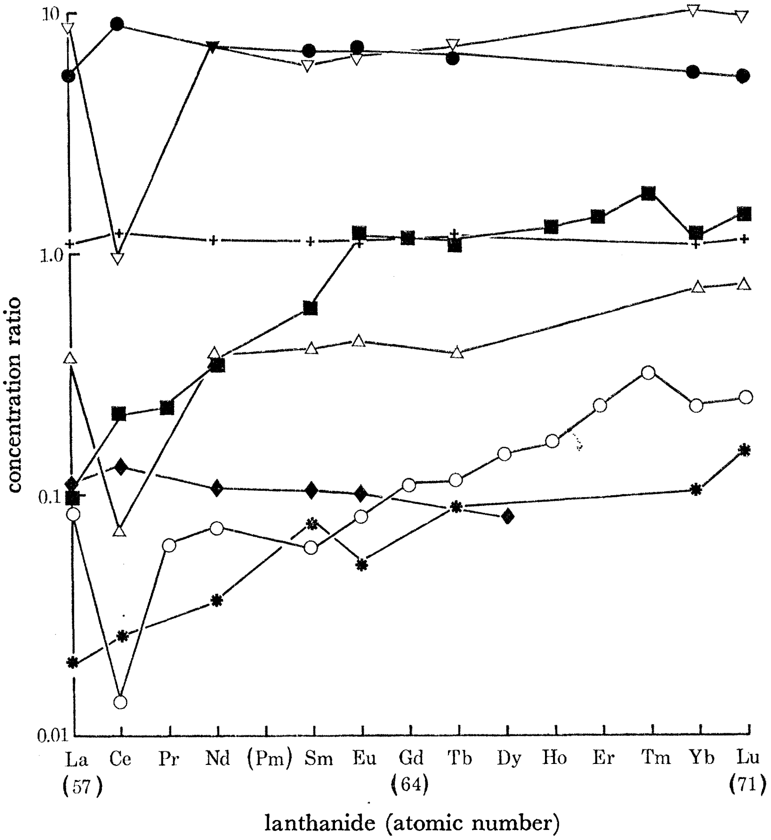

FIGURE 16. Distribution of the lanthanides in ridge-crest ferromanganese deposits (from Piper & Graef 1974; Piper *et al.* 1975; Bonatti *et al.* 1976; Burnett & Piper 1977) nodules and pelagic clay (from Piper 1974*a*), seawater (from Høgdahl *et al.* 1968) and Mid-Atlantic Ridge (M.A.R.) basalt (from Frey & Haskin 1964): ∗, Dellwood Seamount ironstone; ●, ferromanganese nodules; ▽, Galapagos Spreading Centre crust; +, pelagic clay; △, E.P.R. sediment; ■, M.A.R. basalt; ◆, Romanche Trench sulphide; ○, seawater ($10^6 \times$ concentrations). Concentration ratio is the ratio of each individual lanthanide to its concentration in average shale (Piper 1974*a*).

The concentration and isotopic composition of uranium in ridge-crest sediments, rocks and crusts also provide information on the likely sources of elements in such deposits (table 4). Absolute concentrations of U in the sediments are significantly higher than those in pelagic clays (Heye 1969; Fisher & Boström 1969; Bender *et al.* 1971; Veeh & Boström 1971), and the ^{234}U/^{238}U ratio in surface sediments is close to that in seawater, namely 1.15 (Thurber 1962). This probably indicates that the U was derived from seawater by coprecipitation onto Mn and Fe oxyhydroxides (Bender *et al.* 1971; Veeh & Boström 1971).

In ridge-crest crusts and ironstones, the distribution of U appears to fall into two distinct groups. In Mn-rich crusts from the TAG field (M. R. Scott *et al.* 1974), U concentrations are quite high and the ^{234}U/^{238}U ratio is not significantly different from that of seawater, and a similar conclusion has been reached for the Mn crust from the Galapagos Spreading Centre

(Burnett & Piper 1977). In distinct contrast, ridge-crest ironstones have significantly less U than pelagic clays and anomalously high ^{234}U/^{238}U ratios (Veeh & Boström 1971; Piper *et al.* 1975). It appears that whereas the U in the Mn-rich crusts is derived from seawater, that in the ironstones has suffered some fractionation, possibly by the leaching of ^{234}U from basaltic rocks in a hydrothermal system (Rydell & Bonatti 1973). Kazachevskii *et al.* (1964) reported ^{234}U/^{238}U ratios of 1.2 in limonitic precipitates from the Kurile Islands and 1.14 in hydrous Mn and Fe oxide suspensions from the Banu-Wuhu volcano in Indonesia (see Zelenov 1964).

TABLE 4. CONCENTRATIONS OF URANIUM AND ISOTOPIC COMPOSITIONS OF URANIUM, STRONTIUM AND LEAD IN RIDGE-CREST FERROMANGANESE DEPOSITS

deposit	$\frac{\text{U}}{\text{parts}/10^6}$	^{234}U/^{238}U	^{87}Sr/^{86}Sr	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb
E.P.R. sediments	4.16–11.7(1)	1.08–1.14(1)	—	—	—
E.P.R. sediments	4.55–6.90(2)	1.03–1.15(2)	0.708 ± 0.001(2)	18.5$_x$(2,4)	15.543(2)
E.P.R. sediments	0.29–0.71(3)	1.06–1.16(3)	—	—	—
B.D. sediments	1.45–2.14(3)	1.00–1.04(3)	0.70899(10)	18.306(10)	15.518(10)
basal metalliferous sediments	1.97–5.83(4)	0.99–1.04(4)	0.7078–0.7099 ± 0.0001(4)	18.395(4)	15.561(4)
ironstone, AMPH D2	1.25(1)	1.21–1.22(1)	—	—	—
ironstone, AMPH D2	1.25–2.39(5)	1.15–1.23(5)	—	—	—
ironstone, Dellwood Seamount	0.25(6)	1.29(6)	—	—	—
manganese crust Tag area, M.A.R.	9.25–16.46(7)	1.06–1.23(7)	—	—	—
pelagic clays	1–3(8)	0.92(8)	0.72(11)	—	—
seawater	0.003(9)	1.15(9)	0.70906(12)	18.812(14)	15.63(14)
E.P.R. basalt	—	—	0.70248(13)	18.31(15)	15.55(15)

Sources of data: 1, Veeh & Boström (1971); 2, Bender *et al.* (1971); 3, Dymond & Veeh (1975); 4, Dymond *et al.* (1973); 5, Rydell & Bonatti (1973); 6, Piper *et al.* (1977); 7, M. R. Scott *et al.* (1974); 8, Heye (1969); 9, Thurber (1962); 10, Dasch *et al.* (1971); 11, Dasch (1969); 12, Hildreth & Henderson (1971); 13, Hart (1971); 14, Reynolds & Dasch (1971); 15, Tatsumoto (1966).

The isotopic composition of strontium in ridge crest sediments (table 4) has a value similar to that of seawater (Bender *et al.* 1971; Dasch *et al.* 1971). This has also been taken to imply a seawater source for this element, although Dymond *et al.* (1973) have found evidence that exchange of strontium between solid and aqueous phases in 30–90 Ma old basal metalliferous sediments has probably altered the original isotopic composition, thereby obscuring its source.

Available lead isotopic compositions of ridge-crest sediments (table 4) fall in the range exhibited by ocean ridge basalts (Tatsumoto 1966) and are distinctly different from those of ferromanganese nodules, assumed to reflect the seawater ratios. This evidence is thought to indicate an ultimate magmatic or hydrothermal origin for the metalliferous sediments (Bender *et al.* 1971; Dasch *et al.* 1971; Dymond *et al.* 1973), although the data do not allow a distinction to be made between direct precipitation from hydrothermal solutions and other types of solution containing Pb from a magmatic source.

3.3. *Mineralogy*

The mineralogical composition of the oxyhydroxide component of ridge-crest deposits appears to be more variable than that of the nodules. Although the modern E.P.R. sediments were initially described as amorphous (Boström & Peterson 1966), there is some indication from the work of Bagin *et al.* (1975) that goethite and an Fe-rich smectite are both present. In the case of the B.D. sediments, more extensive investigations by Dasch *et al.* (1971), Sayles & Bischoff (1973), Dymond *et al.* (1973), Eklund (1974), Sayles *et al.* (1975) and McMurtry (1975) have established the presence of δ-MnO_2 and todorokite (§2.3.1) in addition to fine-grained goethite (figure 17), and an Fe-rich smectite, probably nontronite.

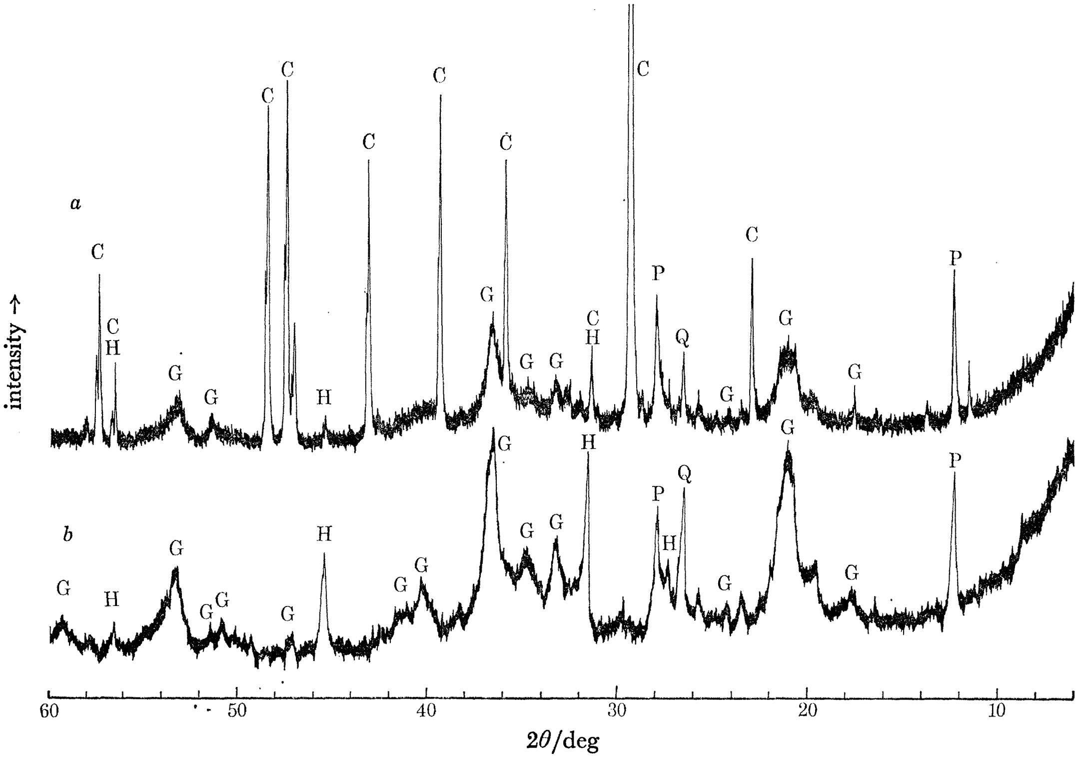

FIGURE 17. X-ray powder diffraction patterns of (*a*) Bauer Deep sediment and (*b*) basal metalliferous sediment (D.S.D.P. site 39). Patterns obtained by ultra-slow scanning, using CuKα radiation and a graphite monochromator. P, Phillipsite; G, goethite; C, calcite; Q, quartz; H, halite. Sample *a* kindly provided by J. Dymond, Oregon State University; sample *b* kindly provided by the Deep Sea Drilling Project, National Science Foundation, Washington, D.C.

Basal metalliferous sediments from the eastern Pacific have also been described as amorphous (von der Borch *et al.* 1971) although subsequent studies have shown the presence of goethite (Dymond *et al.* 1973; Drever 1971) and occasional psilomelane and Fe-rich smectite (Dymond *et al.* 1973). Figure 17 shows the X-ray evidence for the presence of crystalline goethite in such sediments.

Of the two types of ridge-crest rocks and crusts, the Mn-rich variety is reported to contain δ-MnO_2 (Burnett & Piper 1977), birnessite and todorokite (Scott *et al.* 1974; Moore & Vogt 1976) while the ironstones consist of goethite (Bonatti & Joensuu 1966) or X-ray amorphous iron oxyhydroxides (Piper *et al.* 1975).

The main mineralogical contrast between ferromanganese nodules and ridge crest deposits appears to lie in the common occurrence of goethite and the highly variable occurrences of readily identifiable Mn phases in the latter.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

3.4. *Accumulation rates*

The total accumulation rate data in table 5 indicate that the unconsolidated E.P.R. sediments accumulate more rapidly than the B.D. sediments and pelagic clays. The Mn-rich crusts accumulate somewhat more slowly but significantly more rapidly than ferromanganese nodules.

TABLE 5. ACCUMULATION RATES OF FERROMANGANESE DEPOSITS

deposit	sediment accumulation rate	reference or source	metal accumulation rate ng cm^{-2} a^{-1}				reference or source
	µm a^{-1}		Mn	Fe	Cu	Ni	
E.P.R. sediment	9.3–15	1	5800	11000	51	56	7
B.D. sediment	1.4–2.5	2	1100	4400	25	16	7
manganese crust, Tag area, M.A.R.	0.13–0.25	3	13000–24400	20–40	1–3	10–20	8
manganese crust, Galapagos Spreading centre	0.08–2	4	13600	550	13	45	9
nodules	0.0005–> 0.05	5	960	1300	4	14	10
pelagic clays	2	6	500	800	8	10	11

References and sources: 1, Bender *et al.* (1971); Dymond & Veeh (1975); McMurtry (1975); 2, Sayles *et al.* (1975); Dymond & Veeh (1975); McMurty (1975); 3, M. R. Scott *et al.* (1974); 4, Moore & Vogt (1976); Burnett & Piper (1977); 5, figure 9; 6, Ku *et al.* (1968); 7, Dymond & Veeh (1975); 8, calculated by using data from M. R. Scott *et al.* (1974) and assuming a bulk density of 2.5 g cm^{-3}; 9, calculated using data from Moore & Vogt (1976) and assuming a bulk density of 2.5 g cm^{-3}; 10, Kraemer & Schornick (1974); 11, Krishnaswami (1976).

Further distinctions between the various ferromanganese deposits are provided by metal accumulation rates derived from the compositional and sediment accumulation rate data (table 5). The rates for all four metals on the E.P.R. are higher than those in pelagic clays. Manganese accumulation rates in ridge-crest crusts are exceptionally high but the rates for the other metals are of the same order as those for pelagic clays. The close similarity between the accumulation rates of Mn in nodules and sediments has been discussed by Bender *et al.* (1970). Accumulation rates of ridge-crest ironstones are not available.

4. FORMATION OF OCEANIC FERROMANGANESE DEPOSITS

An explanation of the formation of the ferromanganese deposits of the deep sea involves two separate problems. The ultimate sources of the metals in the deposits are of fundamental interest, whereas the modes of accretion of the oxyhydroxide phases on the sea floor, regardless of sources, are of immediate concern. The sources of the metals are considered to be continental denudation and marine volcanism and the relative importance of these two sources had led to considerable controversy since they were first discussed by Murray & Renard (1891). It seems clear that both sources are important (Cronan 1976), since mass balance estimates (Horn & Adams 1966; Boström 1967; Varentsov 1971; Elderfield 1976) indicate that a significant fraction of the Mn in oceanic deposits has a continental source and because recent studies of hydrothermal systems (Ellis 1973) and the reaction between fresh basaltic rock and seawater (Corliss 1971; Hajash 1975; Bischoff & Dickson 1975) show that several metals of concern can be derived from within the ocean basins.

The mode of formation of ferromanganese nodules involes the slow precipitation of oxyhydroxides on exposed solid surfaces, some of which may become nuclei for the formation of concretions. Goldberg & Arrhenius (1958) suggested that a ferric oxide surface could provide an initial reaction site on which seawater MnII could be oxidized by molecular oxygen. Stumm & Morgan (1970) have shown that the precipitation of ferric hydroxide from iron hydroxide species, the forms of importance in seawater (Byrne & Kester 1976), is much more rapid than the precipitation of MnIV oxides at the same pH. The initial deposition of an Fe oxyhydroxide film on foraminiferal and coral surfaces in nodules has been observed by Burns & Brown (1972). The autocatalytic precipitation of Mn oxyhydroxides (Morgan & Stumm 1970; Hem 1976) on such surfaces would then lead to continual accretion of mixed oxyhydroxides from seawater, the rate of deposition being controlled by the rate at which the reactants are brought to the surfaces.

Burns & Brown (1972) suggested that 10 Å manganite (todorokite) may be the first formed Mn-phase on the sea floor which could yield a separate, more oxidized phase (δ-MnO_2), accompanied by dehydration and shrinkage. On the other hand, Burns & Burns (1975) suggested that the epitaxial intergrowth of δ-MnO_2 and FeIII oxyhydroxide is the key to the nucleation of nodule growth and that todorokite forms subsequently under high hydrostatic pressure. This seems unlikely for the reasons given in § 2.3.2.

Some additional insight into the possible modes of formation of oceanic nodules comes from recent work on the chemical and mineralogical compositions of nodules throughout the Pacific Ocean (§ 2.5) and on the modes of formation of nearshore nodules (Calvert & Price 1977*b*). The regional geochemical variation in the Pacific (figures 9–11) led Price & Calvert (1970) to suggest that two distinct mechanisms of formation are involved, a precipitation from normal seawater, which produces a deposit consisting of δ-MnO_2 with roughly equal Mn and Fe and relatively high Ce, Co, Pb and Ti contents, and a diagenetic precipitation producing a deposit consisting of todorokite with more Mn than Fe and high Cu, Ni, Mo and Zn contents. Nearshore nodules, consisting of todorokite, are known to form by the precipitation of remobilized metals from expelled sediment pore waters which has the effect of producing extreme Mn and Fe fractionations (Manheim 1965; Cheney & Vredenburg 1968; Calvert & Price 1970). The explanation of Price & Calvert (1970) was an attempt to extend this mechanism to the abyssal nodules, although it is recognized that anoxic conditions, which promote transition metal mobility in rapidly accumulating nearshore sediments, do not exist in pelagic clays.

Evidence for two distinct modes of precipitation of metals in abyssal nodules is provided, however, by the important observation of Raab (1972) that discoidal nodules from the abyssal northern equatorial Pacific had compositionally distinct upper and lower surfaces. Upper surfaces were enriched in Fe, Co and Pb, while lower surfaces contained more Mn, Ni, Cu, Mo and Zn. Ku & Broecker (1969) and Lalou & Brichet (1972) have also pointed out that upper and lower surfaces of nodules often have distinctly different α-activities and Kunzendorf & Friedrich (1976) observed higher concentrations of U and Th on the surfaces of nodules last exposed to seawater.

Calvert & Price (1977*a*) used the observations of Raab (1972) to suggest that the upper surfaces of the nodules represent precipitation predominantly from seawater whereas the lower surfaces are diagenetic. They further proposed, on the basis of bulk compositions, that there is a continuous variation in the relative proportions of these two sources on a regional scale; the seawater end-member is perhaps best represented by oceanic seamount nodules, which grow slowly on rock or coral substrates, and the diagenetic end-member is represented by the Mn-enriched nodules in the northern equatorial Pacific, which grow significantly more rapidly (figure 8) on a reactive, oxidized sediment substrate. Because of the existence of diagenetic as well as normal seawater metal sources, ultimate sources become obscured.

The distribution of the diagenetic abyssal nodules in the Pacific (figure 9) is clearly controlled by processes taking place in the underlying sediments. Although Price & Calvert (1970) maintained that these nodules form on more rapidly accumulating sediments where diagenetic reaction would more marked, Strakhov (1974*a*) and Piper & Williamson (1977) have shown that the sediments probably accumulate very slowly in these areas, the fractionation of the metals most probably taking place at or close to the sediment surface. This inferred relation between the composition of the nodules and the accumulation rate of the associated sediment has been corroborated by Calvert *et al.* (1978) in a suite of Mn-enriched nodules from a small survey area of the northern equatorial Pacific (figure 18). The mechanism of fractionation of Mn and Fe at the sediment surface is not understood but may involve the reaction of Fe oxyhydroxides with biogenous silica to form a smectite phase in the sediment, as suggested by Lyle *et al.* (1977) who have further proposed that the removal of Fe from the mixed nodular precipitate would facilitate the crystallization of todorokite, the phase in which divalent minor metals are readily accommodated.

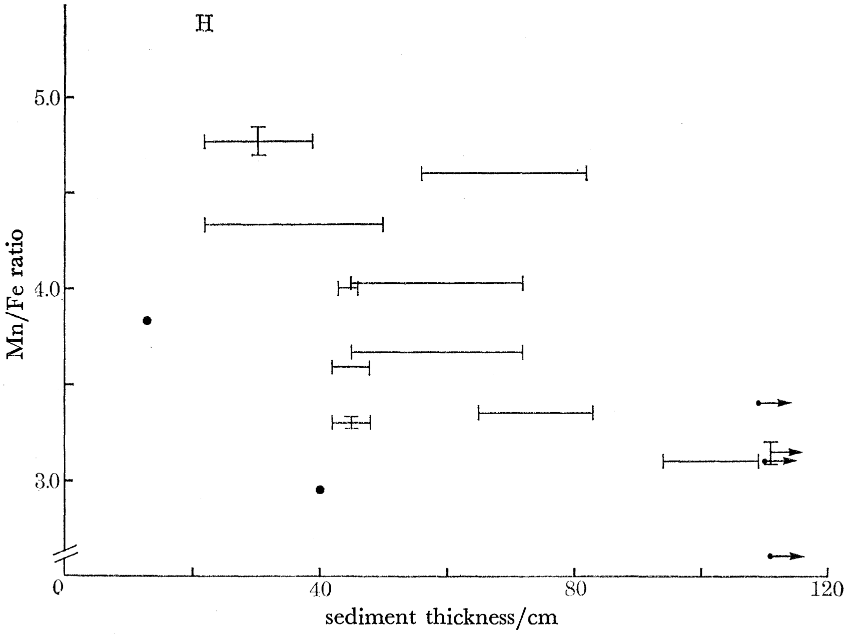

FIGURE 18. Relation between the Mn/Fe ratio of the nodules and the thickness of Quaternary sediment in a small survey area in the northern equatorial Pacific. Horizontal bars indicate the uncertainty in the last appearance of Quaternary radiolarians in the sediments. Vertical bars indicate the range of duplicate analyses of single nodules. Arrows indicate the absence of pre-Quaternary sediment in a core. After Calvert *et al.* (1978).

The relation between the composition of abyssal ferromanganese nodules and their growth rates (§2.4) may provide an alternative explanation for the formation of Mn-enriched nodules in the deep sea. It appears from the work of Heye (1975) that Mn-rich zones in nodules from the northern equatorial Pacific accumulate more rapidly than zones with higher Fe contents.

Hence, nodules with high bulk Mn/Fe ratios may simply represent precipitates which have received additional, relatively rapid impulses of Mn superimposed upon the 'normal' accretion of the mixed Mn and Fe oxyhydroxides from seawater.

The enrichment of Ni and Cu in the Mn-rich nodules from the northern equatorial Pacific (figures 9 and 10) has been explained by their additional supply by settling biological debris (Greenslate *et al.* 1973). This material, mainly skeletal, containing trace metals scavenged from the water column, dissolves on the sediment surface below the lysocline (Adelseck & Berger 1975) thereby releasing a suite of adsorbed and occluded metals (see Piper & Williamson 1977). Determinations of the fluxes of metals to the sea floor by such a process are required to test this hypothesis, but the locations of the zones of transition-metal enriched nodules (figure 9) in areas of high primary biological production in the surface waters of the Pacific (Reid 1962; Koblentz-Mishke *et al.* 1970; El Sayed 1970) are certainly consistent with such an explanation.

The rôle of microorganisms in the precipitation of Mn and Fe on the sea floor has been discussed for a considerable time. Ehrlich (1966) has isolated bacteria from nodules and has suggested that they promote the oxidation of MnII to MnIV (see also Sorokin 1972). Although bacteria are involved in the precipitation of Mn and Fe oxyhydroxides in lakes (Perfil'ev *et al.* 1965) their participation in oxide precipitation in the sea has not been demonstrated. Stumm (in Ehrlich 1964) and Sorokin (1972) have cautioned against the acceptance of biological agencies when compounds that are so readily oxidized inorganically are involved.

Although a direct biological involvement in the formation of ferromanganese nodules remains conjectural, it is clear that microorganisms can play an important part in constructing ferromanganese concretions. Wendt (1974) and Greenslate (1974*a*, *b*) have shown that agglutinating Foraminifera, probably *Saccorhiza*, and other shelter-building organisms, are abundant on the surfaces and in the interiors of some nodules. They have suggested that the skeletal structures of the organisms contribute to the overall growth of nodules and provide a framework in which metal oxyhydroxides can be deposited. A variation on this theme is the suggestion of Monty (1973) that the nodules represent bacterial stromatoliths.

The formation of ferromanganese deposits on the ocean ridge-crest is probably more directly linked to hydrothermal activity at constructive plate margins (Bonatti 1975). The principal features of such deposits, suggesting such an influence, include their rapid accumulation rates and their extreme compositional variability. Moreover, recent work on the thermal régimes at such plate margins (Lister 1972; Spooner & Fyfe 1973; Williams & von Herzen 1974), together with observational (Corliss 1971; Hart 1973) and experimental (Hajash 1975; Bischoff & Dickson 1975; Elderfield *et al.* 1977) studies of the alteration of basaltic rocks by seawater, have suggested that extensive alteration of freshly intruded rock takes place to considerable depths and that the fluxes of metals into the circulating seawater are important in the marine geochemical balance (Wolery & Sleep 1976; see also Strakhov 1974*b*; Elderfield 1976; Lyle 1976). There is at present no report of any direct observation of hydrothermally altered seawater emanating at ocean ridges, although positive temperature anomalies have been recorded in the Tag area of the Mid-Atlantic Ridge (Rona *et al.* 1975) and on the Galapagos Spreading Centre (Detrick *et al.* 1974; Weiss *et al.* 1977). Lupton *et al.* (1977) have recently discovered excess ^{3}He and ^{222}Rn anomalies in water samples collected in high-temperature plumes on the Galapagos Spreading Centre, indicating the hydrothermal origin of the plumes, and Klinkhammer *et al.* (1977) have demonstrated the presence of high concentrations of Mn in these same plumes and in the water over the ridge crest.

In some geothermal areas, such as at Wairakei in New Zealand (Ellis 1970) and in the Reykjanes system in Iceland (Björnsson *et al.* 1972), many features produced by rock/hot water interaction may also be applicable to the mid-ocean ridge setting (Wolery & Sleep 1976). In particular, the circulating fluid, which in Iceland is seawater, contains high concentrations of Mn and Fe. The results of experiments on the hydrothermal alteration of basaltic material by seawater demonstrate that Mn, Fe, Cu and Ni, as well as a wide range of major elements, are released in significant quantities to the aqueous phase (Mottl *et al.* 1974; Hajash 1975; Bischoff & Dickson 1975). On the basis of mass balance estimates, it is thought that such a transfer could account in major part for the mass of metalliferous sediment on the ridge system.

The precipitates from the hydrothermal system are evidently fractionated to a considerable degree. Iron is much more abundant in the unconsolidated sediments and occurs as virtually pure ironstones in some cases. The lanthanide patterns and the U isotopic compositions of these ironstones point to a hydrothermal source. On the other hand, the lanthanides, U and Sr probably have a seawater source in the unconsolidated sediments whereas Pb appears to be magmatic. The sources of the other constituents of the deposits are deduced from their accumulation rates. Thus, Mn is accumulating more rapidly than in pelagic clays in the E.P.R. sediments and in the isolated Mn-rich crusts, although a significant fraction of this element could be derived from seawater in the B.D. For the minor transition metals, Dymond & Veeh (1975) contended that both hydrothermal and seawater sources could be involved; and Heath & Dymond (1977) concluded, on the basis of their partition patterns, that whereas more than 50 % of the Ba, Cu, Ni and Zn are hydrothermal on the E.P.R. significantly more of the Ba and Ni have a seawater source in the B.D.

Discussion of the likely source of P in the E.P.R. sediments shows that evidence for element sources based on accumulation rates can be equivocal. Berner (1973) showed that P is enriched in E.P.R. sediments, deduced that it was also accumulating rapidly at this site and that its source was seawater. Froelich *et al.* (1977) have confirmed these observations by showing that the P is present in the dispersed oxyhydroxide phase and is accumulating approximately 40 times faster on the rise crest than in the B.D. where the rate can be shown to be close to that in pelagic clays. In spite of this high relative rate, which incidentally is even higher than the relative rates for the metals (table 5), Froelich *et al.* (1977) maintain that the P is most probably derived from seawater. The key process involved would appear to be the high sorptive capacity of the poorly ordered oxyhydroxides, which may be derived from hydrothermal solutions, but which scavenge other constituents at a very high rate from circulating seawater. It seems possible that the concentrations of minor transition metals observed in the ridge-crest sediments could also be due to their uptake at high rates from normal seawater by such reactive components. Analyses of the metal contents of hydrothermal solutions at the ridge-crest and some less equivocal methods for identifying ultimate metal sources in the sediments are clearly necessary to resolve this interesting problem.

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Discussion

D. S. Cronan (*Geology Department, Imperial College, London S.W.7, U.K.*). I should like to amplify the reference Dr Calvert made to current work of our group at Imperial College on manganese nodules from the Indian Ocean. We have analysed samples of nodules and encrustations from more than sixty Indian Ocean sites. The results of these analyses coupled with previously published data have shown the existence of an area in the central south equatorial part of the ocean where nodules are very similar in composition to those in the northeastern equatorial Pacific 'ore zone' described by Dr Calvert in that they are rich in Mn, Ni, Cu and Zn (Cronan & Moorby 1976). The sparse data that we have been able to obtain so far on the conditions under which these nodules are forming indicate that they may be similar to those under which the high-grade nodules in the northeastern equatorial Pacific are deposited. The nodules are situated at the margin of the equatorial zone; the few available data on which suggest it to be an area of high biological productivity; their environment of deposition leads to todorokite being their principal mineral phase; and they are often found in association with siliceous sediments. The occurrence of these deposits under conditions seemingly similar to those under which high grade nodules occur in the Pacific should allow us to test the hypotheses which have been proposed to explain the origin of the latter. Furthermore, ongoing work on these deposits will not only help to outline an area of potential mining interest in the Indian Ocean, but should also help in the development of a predictive model which could be used to outline other possible areas of high-grade nodules.

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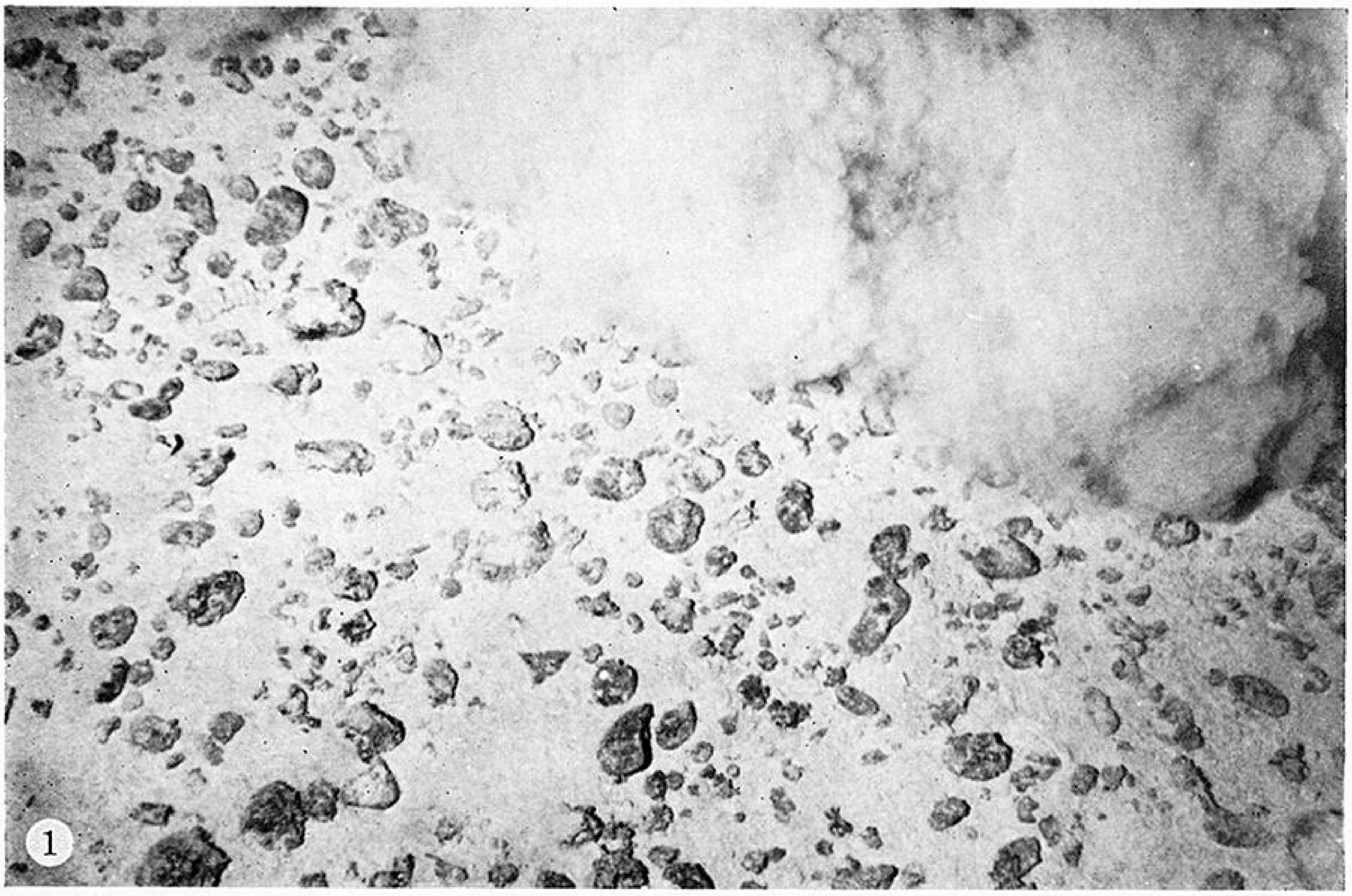

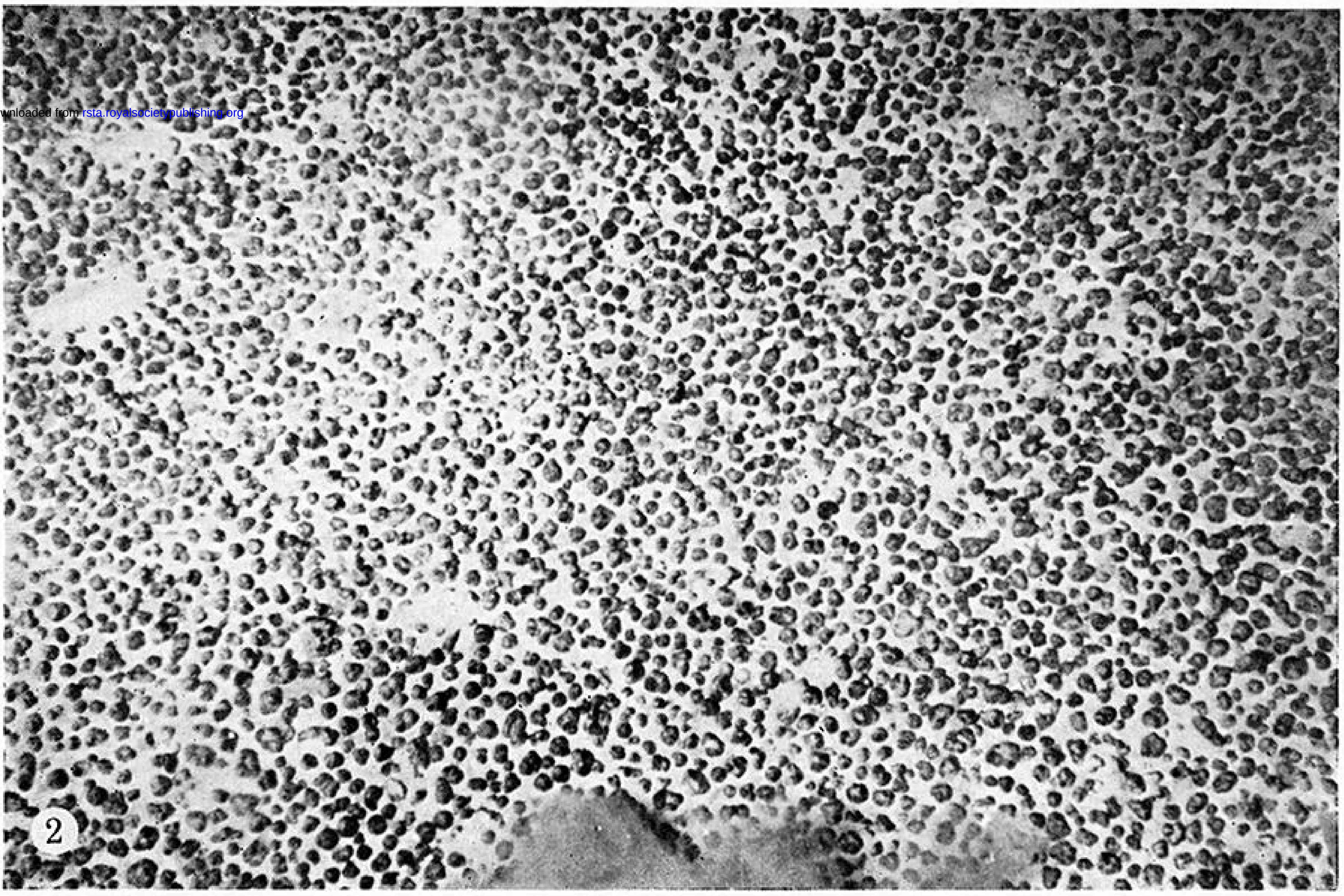

IGURE 1. Sea-floor photograph at 20° 38′ N, 130° 46′ W, depth 5180 m. Nodules are 1–10 cm in diameter and irregular and discoidal in shape; many are partially buried in the fine clay substrate. Sediment cloud was caused by the camera touching the seabed. (U.S. Navy Photo.)

IGURE 2. Sea-floor photograph at 13° 53′ S, 150° 35′ W, depth 3695 m. Nodules are 2–5 cm in diameter and are more or less spherical. The pale-coloured patches are mounds of sediment (calcareous ooze), probably thrown up by benthonic organisms, which cover the nodules. (U.S. Navy Photo.) The distance from the camera to the sea floor is larger in the bottom photograph.