ORIGIN OF MANGANESE NODULE "ORE PROVINCES"

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Summary

Ore grade nodules are enriched in Mn, Ni and Cu. In the Pacific, they occur under waters of intermediate productivity at the margins of the equatorial high productivity zone on sea floor near the CCD. This is thought to result from labile organic matter being supplied by the elevated biological productivity and being concentrated in the sediments near the CCD as a result of calcium carbonate dissolution. The decay of this material promotes diagenetic Mn, Ni and Cu enrichment in nodules. Similar metal enrichments do not appear to occur in Pacific nodules from areas of either higher or lower productivity, the former because abundant biogenic silica replaces calcium carbonate as the main sediment builder at depths near the CCD under highest productivity waters thereby diluting the labile organic material, and the latter due to insufficient diagenetic activity taking place on the sea floor under low productivity waters. In the Indian Ocean, Mn, Ni and Cu rich nodules occur in the Central Indian Ocean Basin. These too are thought to obtain their metals through early diagenetic processes occurring in the sediments. By contrast, similar metal enriching conditions occur less extensively in the Atlantic Ocean and Mn, Ni and Cu, rich nodules appear to be rare there. The close correlation between nodule composition and present day productivity conditions may be due to post depositional changes in nodule composition as productivity conditions change.

Introduction

Marine ferromanganese oxide deposits comprise a triangular continuum, the corners being represented by hydrothermal, hydrogenous (hydrogenetic) and diagenetic deposits respectively. Manganese nodules form a subset within the continuum with continuous mixing from diagenetic end members which contain the mineral 10Å manganite (todorokite) and are enriched in Mn, Ni and Cu, to hydrogenetic end members which contain the mineral δ MnO_2 (vernadite) and are enriched in Fe and Co. The diagenetic deposits receive their metals at least in part from the recycling of elements previously hosted in organic phases on their decay and dissolution, whereas the hydrogenetic deposits receive their metals from normal seawater or unenriched interstitial waters. Ore grade manganese nodules fall near the diagenetic corner of the marine ferromanganese oxide continuum.

Distribution in the Pacific Ocean

Ore grade nodules in the Pacific are generally confined to two zones trending roughly east-west in the tropical regions, which are separated in the eastern Pacific but which converge at about 170° -180°W. They follow the isolines of intermediate biological productivity, strongly suggestive of a biological control on their distribution. Within these zones, the nodules preferentially occupy basin areas. Thus they are found in the Peru Basin, Tiki Basin, Penrhyn Basin, Nova Canton Trough area, Central Pacific Basin and Clarion-Clipperton Zone. Nodules in all these areas have features in common and are suggested to have attained their distinctive composition by similar processes.

Peru Basin

The ore grade manganese nodule field in the Peru Basin, centred on about 7°-8°S, 90°W, is situated on the southern flank of the equatorial zone of high biological productivity. Underlying sediments are largely brown mud with variable amounts of siliceous and calcareous remains. Nodules from near the CCD at around 4250m are characterised by diagenetic growth (enriched in Mn, Ni and Cu) whereas those from shallower depth are characterised mainly by hydrogenetic growth (von Stackelberg, 2000).

Halbach et al (1980) studied the composition of nodules from between 6°-11°S and found large spheroids up to 25cm in diameter with a Mn/Fe ratio >7 and northwards reducing Ni and Cu contents in the north, smaller nodules (3-8cm) with Mn/Fe ratios of 4-7 and Ni + Cu contents up to 2.2% in the middle of the area, and discoidal nodules with a Mn/Fe ratio of <4 and lower Ni and Cu contents in the south. Thus the Mn/Fe ratio increases from south to north as productivity increases, whereas the Ni and Cu contents reach maximum values in the middle of the area where Mn/Fe ratios are about 5.

Tiki Basin

Andrews et al (1983) reported on four sites F, G, H and I in the Tiki Basin, all of which contained Mn, Ni and Cu rich nodules. The sites were located between 5° and 15°S at 134°W on the southern flank and south of the high biological productivity zone. Friedrich et al (1983) additionally reported on sites F and G. There is a decrease in the Mn/Fe ratio of the nodules from 5.5 at the most northerly site to around 2.5 at the other sites. Friedrich et al (1983) report that Ni + Cu at site F (2.54%) is higher than at site G (1.81%). However, all values are above the lower limit expected in diagenetically supplied material.

According to Andrews et al (1983) sediments in the north of the ore grade nodule area are siliceous debris bearing nanno foram ooze above 4550m, passing to siliceous microfossil rich nanno foram mud near 4700m, and mainly siliceous ooze below the CCD. In the south the sediments range from calcareous muds to pelagic clays with increasing depth and there is some evidence for local volcanism.

Penrhyn Basin

Comparisons by Cronan and Hodkinson (1994) of bulk nodule data from the Penrhyn Basin with other Pacific nodule data shows that they fall within the lower and middle parts of the Mn/Fe range for Pacific nodules. However, nodules from the northern part of the Basin where calcareous/siliceous clay predominates have the highest Mn/Fe ratio and highest Ni and Cu concentrations, (although they decrease slightly as the equator is approached) reflecting diagenetic supply of metals to them. Superimposed on this trend are variations in nodule composition with their distance above or below the CCD. In the Mn, Ni and Cu rich nodule area, maximum values of these metals in nodules occur within about 200m of the CCD. Thus, although overall maxima in Mn, Ni and Cu occur in the latitudinal range where diagenetically formed 10Å manganite predominates (2-6°S) there is a very wide scatter of metal values within this latitudinal range which diminishes both to the north and south where, respectively, siliceous ooze and pelagic clay sedimentation prevail. This may be explained by the varying composition of nodules with distance from the CCD under the high productivity area. The latitudinal variation in Mn, Ni and Cu in Penrhyn Basin nodules may thus be due to there being a hydrogenous Mn, Ni and Cu poor source of these metals throughout the Basin, superimposed on which is a major diagenetic source of them between about 2° and 6°S at depths near the CCD, but less so in the very north of the Basin (0-2°S) where siliceous sedimentation prevails under highest productivity waters.

Phoenix Islands - Nova Canton Trough Area

The Phoenix Islands EEZ and Nova Canton Trough nodule area is centred approximately on 2°S, 168°W in water depths of 5200-5600m. It lies on the southern margin of the high biological productivity zone where it is narrowing westwards. The Mn, Ni, and Cu rich nodules are situated within the north-eastern part of the Phoenix Islands EEZ where it abuts the Nova Canton Trough (Cronan and Hodkinson, 1991). Underlying sediments consist largely of siliceous clay in the northern part of the area under the highest productivity waters and brownish pelagic clay in the southern region.

Manganese concentrations in the nodules are at a maximum of >25% between the equator and 2.5°S, where the Mn/Fe ratio is also highest. Manganese shows a tendency to decrease towards the south. Nickel and copper show similar trends to Mn, with maximum values of these elements of about 1.5% of each being centred just south of the equator. Northern area nodules are characterised by diagenetic growth whereas southern area nodules are characterised by hydrogenetic growth. Maximum abundances of Ni and Cu occur between 5300-5500m just below the CCD (MMAJ, 1988).

Central Pacific Basin

Usui (1984) described manganese nodules from a transect between Wake Island and Tahiti, part of which passed through the Central Pacific Basin. In the central part of the area, between the Magellan Trough (10°N, 176°W) and the Nova Canton Trough (1°S, 167°W), diagenetic nodules were found associated with siliceous ooze and clay sedimentation below the CCD. These nodules had an average Mn/Fe ratio of about 4 (max 9.9) and contained the highest mean concentrations of Mn (24.3%), Ni (1.23%) and Cu (1.18%) found on the transect.

Within the Central Pacific Basin, Ni and Cu increase south-eastwards from the Magellan Trough to a maximum at about 2.5°-3°N and then decrease again towards the equator where productivity is highest. Clearly, these observations show similarities with those from some areas to the south of the equator in that Ni and Cu increase from low productivity areas towards the high productivity areas, but then decrease again as maximum productivity is approached on the equator.

Clarion-Clipperton Zone

Much has been written about the CC Zone nodules (see Morgan 2000 for a review) and thus only the briefest summary is needed here. The deposits rest largely below the CCD on siliceous ooze and pelagic clay. The axis of highest average Mn/Fe ratio (5), and Mn (>30%), Ni (1.4%) and Cu (1.2%) concentrations runs roughly SW-NE from 5°N, 145°W to 15°N, 130°W (Morgan, 2000) with values of these elements decreasing both to the N and S as productivity respectively declines to the north and increases towards the equatorial maximum in the south. Thus, in keeping with many of the similar deposits described above, they occur on the flanks of the high productivity zone, not in its centre.

Indian Ocean

According to Jauhari and Pattan (2000), three types of nodules are present in the Central Indian Ocean Basin, a diagenetic type rich in 10Å manganite, a hydrogenetic type rich in δ MnO_2 and a mixed type. The diagenetic type has a high Mn/Fe ratio (up to about 6.5) and high Ni and Cu contents and rests on siliceous sediments below the CCD (which is at around 5000m) in the high productivity area in the north of the Basin between about 5°-15°. It is replaced in the south by nodules of hydrogenetic type that are poorer in Mn, Ni and Cu, resting on pelagic clay under less productive waters. This pattern shows features in common with some areas in the Pacific described above, in that the deposits show north-south compositional variability and highest grades occur below the CCD. North of 5°N, terrigenous sediments from the major S.E. Asian river systems become increasingly important and the nodule abundances and grades suffer accordingly.

Atlantic Ocean

Diagenetic Mn, Ni and Cu rich nodules occur most notably in the Angola Basin and less so in the Cape/Agulhas Basin and the East Georgia Basin. According to Kasten et al (1998) and references therein, in the Angola Basin, the nodules average 0.91% Ni and 0.52% Cu with a Mn/Fe ratio of 2.6, while in the Cape Basin maximum values are around 1.8% Ni + Cu with a Mn/Fe ratio of

3.2. In the East Georgia Basin, Mn/Fe ratios of between 2.9 and 3.4 occur. These three areas have elevated biological productivity in common and elevated organic carbon contents in their sediments (Berger and Herguera, 1992), which coupled with their depth near or below the CCD would help to explain the composition of their nodules. However, Ni and Cu are lower in them than in areas of diagenetic nodules in the Pacific and Indian Oceans. Over much of the remainder of the Atlantic the sea floor is above the CCD which, coupled with high detrital inputs, is not conducive to the formation of diagenetic Ni and Cu rich nodules.

Discussion

Cronan and Hodkinson (1994) and Cronan (1997) developed a model to explain the compositional variability of nodules in the Penrhyn Basin which can be summarised as follows. Under the flanks of the high productivity area, reduced sedimentation rates due to calcium carbonate dissolution near the CCD enhance the content of organic carbon bearing phases (faecal material, marine snow, etc) in the sediments there, the decay of which drives the diagenetic reactions that promote 10Å manganite and Mn, Ni and Cu enrichment in the nodules. Away from the CCD, organic carbon concentrating processes are less effective. South of about 6°S as productivity declines there is probably insufficient organic carbon supplied to the sea floor to promote the formation of diagenetic nodules at any depth. North of about 2°S, siliceous ooze replaces pelagic clay as the main sediment builder at and below the CCD, and its high rate of accumulation dilutes the concentrations of organic material at all depths to levels below that at which diagenetic Mn, Ni and Cu rich nodules can form.

To a greater or lesser extent, this model can account for much of the variability in nodule composition found in the other South Pacific areas described here, although local factors may modify the general model outlined above. In the Peru Basin, as in the Penrhyn Basin, diagenetic Mn, Ni and Cu rich nodules are concentrated near the CCD and their Ni and Cu contents peak south of the highest productivity waters. In the Tiki Basin, greatest diagenetic influences are also found in the north of the Basin. As the S.Pacific basins deepen to the west, more of the sea floor is below the CCD and the areas of diagenetic nodules tend also to occur below the CCD as, for example, in the Phoenix Islands -Nova Canton Trough area. This may be because the settling rates of large organic particles are quite fast in the deep ocean. For example, Berger and Wefer (1992) report that the flux of organic matter is similar at 4000m to that at 2000m. Probably only limited decay of this material takes place between it settling through the CCD and reaching the sea floor, although these authors imply that more could take place during its resuspension in the Benthic Boundary and Nepheloid Layers. Nevertheless, enough probably gets sedimented to extend the depth of diagenetic nodule formation to well below the CCD under high productivity areas of limited siliceous sediment accumulation.

In the North Pacific, the trends in nodule composition in relation to the equatorial zone are reversed. Thus in both the Central Pacific Basin and the Clarion-Clipperton Zone the highest nodule grades occur in diagenetic nodules on the northern flanks of the high productivity area and decline both to the north and south. The general model erected to explain the Penrhyn Basin nodule variability thus probably applies, at least in part, to these areas also.

The model has less applicability in the Indian Ocean than in the Pacific and even less in the Atlantic. In the Indian Ocean, diagenetic nodules associated with sediments containing moderate amounts of organic carbon, as in the Penrhyn Basin, occur to the south of the equatorial zone in the CIOB. Farther to the south these nodules give way to hydrogenetic varieties, as also in the Penrhyn Basin. However, to the north the changes in nodule composition that might be expected under higher productivity waters do not occur because terrigenous sedimentation becomes important in those areas (Jauhari and Pattan, 2000) which reduces both nodule abundance and grade. In the Atlantic, the influence of equatorial high productivity on nodule composition evident in the other two oceans is not seen, mainly because the equatorial area of high productivity is largely floored with carbonate sediments. Where diagenetic nodules do occur, as in the Angola, Cape and E.Georgia Basins, productivity is also elevated but the sea floor is near or below the CCD leading to reduced sedimentation rates.

The role of siliceous sedimentation in influencing nodule composition has been discussed by Friedrich et al (1983) who proposed that the dissolution of siliceous organisms can lead to the liberation of Mn, Ni and Cu into interstitial waters and their uptake into forming nodules. However, the observations in the preceding sections point to a seeming paradox in this regard. For example, siliceous sedimentation in the Penrhyn Basin between 0-2°S appears to inhibit Mn, Ni and Cu uptake in the nodules there, whereas in the CCZ to the NE some of the highest concentrations of these metals in Pacific nodules occur in those resting on siliceous sediments. The resolution of this paradox may lie in the rate of accumulation of the siliceous sediments rather than in their composition. Friedrich et al (1983) note that siliceous sediment accumulation rates in the CCZ have been low since Miocene times. This could have led to organic material being concentrated in them near and below the CCD, as outlined for the sub-equatorial Penrhyn Basin (2°-6°S) by Cronan and Hodkinson (1994), and the nodules resting on them accordingly being enriched in diagenetically supplied metals. By contrast, in the equatorial Penrhyn Basin (0-2°S), siliceous sedimentation rates appear to be too high for this to take place. Nevertheless, some supply of metals to nodules from biogenic silica dissolution cannot be ruled out, but that from organic carbon related decay is probably greater (Aplin and Cronan, 1985).

A second apparent paradox in regard to nodule compositional variability in relation to biological productivity is that bulk nodule compositions appear to reflect modern productivity conditions, and yet the nodules themselves have been forming over quite long periods of time. During these long periods, in some cases since the Miocene, environmental conditions must have varied and certainly could have been different from those prevailing today. Berger and Herguera (1992) present compelling evidence for productivity changes in the equatorial Pacific between glacial and postglacial time by a factor of about 2. Are these reflected in the composition of the underlying nodules? In order to answer this question, detailed layer by layer studies on the nodules would be needed. However, an alternative possibility is that post-depositional changes in nodule composition over time can result in their "equilibrating" with current depositional conditions. The open porous nature of the nodule structure would lend itself to exchange reactions between dissolved species in the nodule and sediment interstitial waters (the former frequently comprising 20% or more of the in-situ nodule) and elements in the solid phases. It has been shown from Sr isotope studies that there is exchange of Sr with seawater in some ferromanganese oxides (Ingram et al, 1990). Additionally, some evidence for transition metal exchange between the solid phase of ferromanganese oxides and sediment interstitial waters is forthcoming from unpublished studies carried out at Imperial College by the writer and colleagues on ferromanganese oxide crusts from the S.W. Pacific. During leg 135 of the ODP, some buried hydrothermal crusts were recovered in the Lau Basin. In comparison with modern hydrothermal crusts from the region they are enriched in several elements, including Ni and Cu. These compositional differences are thought to be due to the element enrichments in the buried crusts having occurred post deposition. Consequent on their porous nature the most likely mechanism for post depositional compositional change in them is the uptake of minor elements from the interstitial waters of the sediments in which they occur. A lack of any clear compositional trend in the buried crusts with age (from 0.2-3.5 my) would indicate that duration of burial has had little effect on their composition. Further, that the youngest of the crusts is only 0.2 my old suggests that the process of diagenetic minor element uptake from interstitial waters must have occurred near the sediment surface relatively soon after deposition. If these results can be extrapolated to the manganese nodules discussed in the present work, the correlation between their composition and present day depositional conditions would be explained.

References

Andrews, J.E. et al, 1983. The Hawaii-Tahiti transect: the oceanographic environment of manganese nodule deposits in the Central Pacific. Mar. Geol. 54, 109-130.

Aplin, A. and Cronan, D.S., 1985. Ferromanganese oxide deposits from the Central Pacific Ocean II – nodules and associated sediments. Geochim. et Cosmochim. Acta, 49, 437-451.

Berger, W.H. and Herguera, J.C., 1992. Reading the sedimentary record of the ocean's productivity. In: Falkowski, P.G. & Woodhead, A.D. (Eds), Primary Productivity and Biogeochemical Cycles in the Sea, Plenium Press, 455-486, New York.

Berger, W.H. and Wefer, G., 1992. Flux of biogenous materials to the seafloor: open questions. In: Hsu, K.J. and Thiede, J. (Eds), Use and Misuse of the Seafloor, John Wiley, 285-318, Chichester.

Cronan, D.S., 1997. Some controls on the geochemical variability of manganese nodules with particular reference to the tropical South Pacific. In: Geol. Soc. Lond., Spec. Publ. 119, 139-151.

Cronan, D.S. and Hodkinson, R.A., 1991. An evaluation of Mn nodules and Co rich crusts in S. Pacific EEZs: Part 2. Mar. Min. 10, 267-284.

Cronan, D.S. and Hodkinson, R.A., 1994. Element supply to surface manganese nodules along the Aitutaki-Jarvis Transect, South Pacific, Jl. Geol. Soc. Lond. 151, 391-401.

Friedrich, G. et al, 1983. Morphological and geochemical characteristics of manganese nodules collected from three areas on an equatorial Pacific transect by R.V. Sonne. Mar. Min., 4, 167-253.

Halbach, P. et al, 1980. Regional variations in Mn, Ni, Cu and Co of ferromanganese nodules from a basin in the S.E. Pacific. Mar. Geol. 38, M1-M9.

Ingram, B.L. et al, 1990. Age determinations and growth rates of Pacific ferromanganese deposits using Sr isotopes. Geochim. Cosmochim. Acta, 54, 1709-1721.

Jauhari, P. and Pattan, J.N., 2000. Ferromanganese nodules from the Central Indian Ocean Basin. In: Cronan, D.S. (Ed). Handbook of Marine Mineral Deposits, CRC Press, 171-195, Boca Raton.

Kasten, S. et al, 1998, REE in Mn nodules from the S. Atlantic as indicators of ocean bottom water flow. Mar. Geol. 146, 33-52.

Metal Mining Agency of Japan, 1988. Ocean Resources Investigation in the Sea Area of Republic of Kiribati, JICA-MMAJ, 184pp, Tokyo.

Morgan, C.L., 2000. Resource estimates of the Clarion-Clipperton manganese nodule deposits. In: Cronan, D.S. (Ed), Handbook of Marine Mineral Deposits, CRC Press, 145-170, Boca Raton.

Usui, A., 1984. Regional variation of manganese nodule facies on the Wake-Tahiti Transect: morphological, chemical and mineralogical study. Mar. Geol. 54, 27-51.

von Stackleberg, U., 2000. Manganese nodules of the Peru Basin. In: Cronan, D.S. (Ed), Handbook of Marine Mineral Deposits, CRC Press, 197-238, Boca Raton.