MANATEES

See **MARINE MAMMAL OVERVIEW**

MANGANESE NODULES

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Introduction

Manganese nodules, together with micronodules and encrustations, are ferromanganese oxide deposits which contain variable amounts of other elements (**Table 1**). They occur throughout the oceans, although the economically interesting varieties have a much more restricted distribution. Manganese nodules are spherical to oblate in shape and range in size from less than 1 cm in diameter up to 10 cm or more. Most accrete around a nucleus of some sort, usually a volcanic fragment but sometimes biological remains.

The deposits were first described in detail in the Challenger Reports. This work was co-authored by J. Murray and A. Renard, who between them initiated the first great manganese nodule controversy. Murray believed the deposits to have been formed by submarine volcanic processes whereas Renard believed that they had precipitated from continental runoff products in sea water. This controversy remained unresolved until it was realized that nodules could obtain their metals from either or both sources. The evidence for this included the finding of abundant nodules in the Baltic Sea where there are no volcanic influences, and the finding of rapidly grown ferromanganese oxide crusts associated with submarine hydrothermal activity of volcanic origin on the Mid-Atlantic Ridge. Subsequently, a third source of metals to the deposits was discovered, diagenetic remobilization from underlying sediments. Thus marine ferromanganese oxides can be represented on a triangular diagram (**Figure 1**), the corners being occupied by hydrothermal (volcanically derived), hydrogenous (seawater derived) and diagenetic (sediment interstitial water derived) constituents.

There appears to be a continuous compositional transition between hydrogenous and diagenetic deposits, all of which are formed relatively slowly at normal deep seafloor temperatures. By contrast, although theoretically possible, no continuous compositional gradation has been reported between hydrogenous and hydrothermal deposits, although mixtures of the two do occur. This may be partly because (1) the growth rates of hydrogenous and hydrothermal deposits are very different with the latter accumulating much more rapidly than the former leading to the incorporation of only limited amounts of the more slowly accumulating hydrogenous material in them, and (2) the temperatures of formation of the deposits are different leading to mineralogical differences between them which can affect their chemical composition. Similarly, a continuous compositional gradation between hydrothermal and diagenetic ferromanganese oxide deposits has not been found, although again this is theoretically possible. However, the depositional conditions with which the respective deposits are associated i.e., high temperature hydrothermal activity in mainly sediment-free elevated volcanic areas on the one hand, and low-temperature accumulation of organic rich sediments in basin areas on the other, would preclude much mixing between the two.

Figure 1 Triangular representation of marine ferromanganese oxide deposits.

Possibly they may occur in sedimented active submarine volcanic areas.

Internal Structure

The main feature of the internal structure of nodules is concentric banding which is developed to a greater or lesser extent in most of them (**Figure 2**). The bands represent thin layers of varying reflectivity in polished section, the more highly reflective layers being generally richer in manganese than the more poorly reflective ones. They are thought to possibly represent varying growth conditions.

On a microscopic scale, a great variety of structures and textures are apparent in nodules, some of them indicative of postdepositional alteration of nodule interiors. One of the most commonly observed and most easily recognizable is that of collomorphic globular segregations of ferromanganese oxides on a scale of tenths of a millimeter or less, which often persist throughout much of the nodule interior. Often the segregations become linked into polygons or cusps elongated radially in the direction of growth of the nodules. Several workers have also recognized organic structures within manganese nodules. Furthermore, cracks and fissures of various sorts are a common feature of nodule interiors.

Figure 2 Concentric banding in a manganese nodule. (Reproduced by kind permission of CNEXO, France.)

Fracturing of nodules is a process which can lead to their breakup on the seafloor, in some cases as a result of the activity of benthic organisms, or of bottom currents. Fracturing is an important process in limiting the overall size of nodules growing under any particular set of conditions.

Growth Rates

It is possible to assess the rate of growth of nodules either by dating their nuclei, which gives a minimum rate of growth, or by measuring age differences between their different layers. Most radiometric dating techniques indicate a slow growth rate for nodules, from a few to a few tens of millimeters per million years. Existing radiometric and other techniques for nodule dating include uranium series disequilibrium methods utilizing ²³⁰Th ²³¹Pa, the ¹⁰Be method, the K-Ar method, fission track dating of nodule nuclei, and hydration rind dating.

In spite of the overwhelming evidence for slow growth, data have been accumulating from a number of sources which indicate that the growth of nodules may be variable with periods of rapid accumulation being separated by periods of slower, or little or no growth. In general, the most important factor influencing nodule growth rate is likely to be the rate at which elements are supplied to the deposits, diagenetic sources generally supplying elements at a faster rate than hydrogenous sources (**Figure 1**). Further, the tops, bottoms and sides of nodules do not necessarily accumulate elements at the same rate, leading to the formation of asymmetric nodules in certain circumstances (**Figure 3**). Differences in the surface morphology between the tops, bottoms and sides of nodules *in situ* may also be partly related to growth rate differences. The tops receive slowly accumulating elements hydrogenously supplied from seawater and are smooth, whereas the bottoms receive more rapidly accumulating elements diagenetically supplied from the interstitial waters of the sediments and are rough (**Figure 3**). The 'equatorial bulges' at the sediment-water interface on some nodules have a greater abundance of organisms on them than elsewhere on the nodule surface, suggesting that the bulges may be due to rapid growth promoted by the organisms.

It is evident therefore that nodule growth cannot be regarded as being continuous or regular. Nodules may accrete material at different rates at different times and on different surfaces. They may also be completely buried for periods of time during which it is possible that they may grow from interstitial waters at rates different from those while on the

Figure 3 Morphological and compositional differences between the top and bottom of a Pacific nodule. (Reproduced with permission from Cronan, 1980.)

surface, or possibly not grow at all for some periods. Some even undergo dissolution, as occurs in the Peru Basin where some nodules get buried in suboxic to reducing sediments.

Distribution of Manganese Nodules

The distribution and abundance of manganese nodules is very variable on an oceanwide basis, and can also be highly variable on a scale of a kilometer or less. Nevertheless, there are certain regional regularities in average nodule abundance that permit some broad areas of the oceans to be categorized as containing abundant nodules, and others containing few nodules (**Figure 4**), although it should always be borne in mind that within these regions local variations in nodule abundance do occur.

The distribution of nodules on the seafloor is a function of a variety of factors which include the presence of nucleating agents and/or the nature and age of the substrate, the proximity of sources of elements, sedimentation rates and the influence of organisms. The presence of potential nuclei on the seafloor is of prime importance in determining nodule distribution. As most nodule nuclei are volcanic in origin, patterns of volcanic activity and the subsequent dispersal of volcanic materials have an important influence on where and in what amounts nodules occur. Other materials can also be important as nodule nuclei. Biogenic debris such as sharks' teeth, can be locally abundant in areas of slow sedimentation and their distribution will in time influence the abundance of nodules in such areas.

As most nuclei are subject to replacement with time, old nodules have sometimes completely replaced their nuclei and have fractured, thus providing abundant nodule fragments to serve as fresh nuclei for ferromanganese oxide deposition. In this way, given sufficient time, areas which initially contained only limited nuclei may become covered with nodules.

Figure 4 Distribution of manganese nodules in the oceans (updated from Cronan, 1980 after various sources.) ..., Areas of nodule coverage; \mathfrak{m} , areas where nodules are locally abundant.

One of the most important factors affecting nodule abundance on the seafloor is the rate of accumulation of their associated sediments, low sedimentation rates favoring high nodule abundances. Areas of the seafloor where sedimentation is rapid are generally only sparsely covered with nodules. For example, most continental margin areas have sedimentation rates that are too rapid for appreciable nodule development, as do turbiditefloored deep-sea abyssal plains. Low rates of sedimentation can result either from a minimal sediment supply to the seafloor or currents inhibiting its deposition. Large areas in the centers of ocean basins receive minimal sediment input. Under these conditions substantial accumulation of nodules at the sediment surface is favored.

Worldwide Nodule Distribution Patterns

Pacific Ocean As shown in **Figure 4**, nodules are abundant in the Pacific Ocean in a broad area, called the Clarion-Clipperton Zone, between about 6° N and 20° N, extending from approximately 120° W to 160° W. The limits of the area are largely determined by sedimentation rates. Nodules are also locally abundant further west in the Central Pacific Basin. Sediments in the northern part of the areas of abundant nodules in the North Pacific are red clays with accumulation rates of around 1 mm per thousand years whereas in the south they are siliceous oozes with accumulation rates of 3 mm per thousand years, or more.

Nodule distribution appears to be more irregular in the South Pacific than in the North Pacific, possibly as a result of the greater topographic and sedimentological diversity of the South Pacific. The nodules are most abundant in basin environments such as those of the south-western Pacific Basin, Peru Basin, Tiki Basin, Penrhyn Basin, and the Circum-Antarctic area.

Indian Ocean In the Indian Ocean the most extensive areas of nodule coverage are to the south of the equator. Few nodules have been recorded in the Arabian Sea or the Bay of Bengal, most probably because of the high rates of terrigenous sediment input in these regions from the south Asian rivers. The equatorial zone is also largely devoid of nodules. High nodule concentrations have been recorded in parts of the Crozet Basin, in the Central Indian Ocean Basin and in the Wharton Basin.

Atlantic Ocean Nodule abundance in the Atlantic Ocean appears to be more limited than in the Pacific or Indian Oceans, probably as a result of its relatively high sedimentation rates. Another feature which inhibits nodule abundance in the Atlantic is that much of the seafloor is above the calcium carbonate compensation depth (CCD). The areas of the Atlantic where nodules do occur in appreciable amounts are those where sedimentation is inhibited. The deep water basins on either side of the Mid-Atlantic Ridge which are below the CCD and which accumulate only limited sediment contain nodules in reasonable abundance, particularly in the western Atlantic. Similarly, there is a widespread occurrence of nodules and encrustations in the Drake Passage– Scotia Sea area probably due to the strong bottom currents under the Circum-Antarctic current inhibiting sediment deposition in this region. Abundant nodule deposits on the Blake Plateau can also be related to high bottom currents.

Buried nodules Most workers on the subject agree that the preferential concentration of nodules at the sediment surface is due to the activity of benthic organisms which can slightly move the nodules. Buried nodules have, however, been found in all the oceans of the world. Their abundance is highly variable, but it is possible that it may not be entirely random. Buried nodules recovered in larger diameter cores are sometimes concentrated in distinct layers. These layers may represent ancient erosion surfaces or surfaces of nondeposition on which manganese nodules were concentrated in the past. By contrast, in the Peru Basin large asymmetrical nodules get buried when their bottoms get stuck in tenacious suboxic sediment just below the surface layer.

Compositional Variability of Manganese Nodules

Manganese nodules exhibit a continuous mixing from diagenetic end members which contain the mineral 10Å manganite (todorokite) and are enriched in Mn, Ni and Cu, to hydrogenous end members which contain the mineral δ MnO₂ (vernadite) and are enriched in Fe and Co. The diagenetic deposits derive their metals at least in part from the recycling through the sediment interstitial waters of elements originally contained in organic phases on their decay and dissolution in the sediments, whereas the hydrogenous deposits receive their metals from normal sea water or diagenetically unenriched interstitial waters. Potentially ore-grade manganese nodules of resource interest fall near the diagenetic end member in composition. These are nodules that are variably enriched in Ni and Cu, up to a maximum of about 3.0% combined.

	Pacific Ocean	Atlantic Ocean	Indian Ocean	Southern Ocean	World Ocean Crustal average	abundance	Enrichment factor	Shallow marine	Lakes
В	0.0277	$=$		$\overline{}$		0.0010	27.7		
Na	2.054	1.88			1.9409	2.36	0.822	0.81	0.22
Mg	1.710	1.89			1.8234	2.33	0.782	0.55	0.26
Al	3.060	3.27	2.49		2.82	8.23	0.342	1.80	1.16
Si	8.320	9.58	11.40		8.624	28.15	0.306	8.76	5.38
P	0.235	0.098			0.2244	0.105	2.13	0.91	0.15
Κ	0.753	0.567	\equiv		0.6427	2.09	0.307	1.30	0.40
Ca	1.960	2.96	2.37		2.47	4.15	0.595	2.40	1.14
Sc	0.00097					0.0022	0.441		
Τi	0.674	0.421	0.662	0.640	0.647	0.570	1.14	0.212	0.338
V	0.053	0.053	0.044	0.060	0.0558	0.0135	4.13	0.012	0.001
Cr	0.0013	0.007	0.0029	\equiv	0.0035	0.01	0.35	0.002	0.006
Mn	19.78	15.78	15.10	11.69	16.02	0.095	168.6	11.88	12.61
Fe	11.96	20.78	14.74	15.78	15.55	5.63	2.76	21.67	21.59
Co	0.335	0.318	0.230	0.240	0.284	0.0025	113.6	0.008	0.013
Ni	0.634	0.328	0.464	0.450	0.480	0.0075	64.0	0.014	0.022
Cu	0.392	0.116	0.294	0.210	0.259	0.0055	47.01	0.002	0.003
Zn	0.068	0.084	0.069	0.060	0.078	0.007	11.15	0.011	0.051
Ga	0.001					0.0015	0.666		
Sr	0.085	0.093	0.086	0.080	0.0825	0.0375	2.20		
Y	0.031					0.0033	9.39	0.002	0.002
Zr	0.052			0.070	0.0648	0.0165	3.92	0.004	0.045
Mo	0.044	0.049	0.029	0.040	0.0412	0.00015	274.66	0.004	0.003
Pd	0.602^{-6}	$0.574 - 6$	$0.391 - 6$	$\overline{}$	0.553^{-6}	0.665^{-6}	0.832		
Ag	0.0006	\equiv		$\overline{}$		0.000007	85.71		
Cd	0.0007	0.0011			0.00079	0.00002	39.50		
Sn	0.00027					0.00002	13.50		
Te	0.0050								
Ba	0.276	0.498	0.182	0.100	0.2012	0.0425	4.73	0.287	0.910
La	0.016					0.0030	5.33		0.027
Yb	0.0031					0.0003	10.33		
W	0.006		$\overline{}$			0.00015	40.00		
Ir	0.939^{-6}	0.932^{-6}		$\overline{}$	0.935^{-6}	0.132^{-7}	70.83		
Au	0.266^{-6}	0.302^{-6}	$0.811-7$		0.248^{-6}	0.400^{-6}	0.62		
Hg	0.82^{-4}	0.16^{-4}	0.15^{-6}		0.50^{-4}	0.80^{-5}	6.25		
ΤI	0.017	0.0077	0.010		0.0129	0.000045	286.66		
Pb	0.0846	0.127	0.093		0.090	0.00125	72.72	0.002	0.063
Bi	0.0006	0.0005	0.0014	$\overline{}$	0.0008	0.000017	47.05		

Table 1 Average abundances of elements in ferromanganese oxide deposits

Note: Superscript numbers denote powers of ten, e.g.⁻⁶ = \times 10⁻⁶. Reproduced with permission from Cronan (1980).

One of the most striking features shown by chemical data on nodules are enrichments of many elements over and above their normal crustal abundances (**Table 1**). Some elements such as Mn, Co, Mo and Tl are concentrated about 100-fold or more; Ni, Ag, Ir and Pb are concentrated from about 50- to 100-fold, B, Cu, Zn, Cd, Yb, W and Bi from about 10- to 50-fold and P, V, Fe, Sr, Y, Zr, Ba, La and Hg up to about 10-fold above crustal abundances.

Regional Compositional Variability

Pacific Ocean In the Pacific, potentially ore-grade nodules are generally confined to two zones running roughly east-west in the tropical regions, which are well separated in the eastern Pacific but which converge at about 170°–180°W (**Figure 5**). 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 near or below the CCD. Thus they are found in the Peru Basin, Tiki Basin, Penrhyn Basin, Nova Canton Trough area, Central Pacific Basin and Clarion-Clipperton Zone (Figure **5**). Nodules in all these areas have features in common and are thought to have attained their distinctive composition by similar processes.

The potentially ore-grade manganese nodule field in the Peru Basin, centered at about $7^{\circ}-8^{\circ}S$ and

Figure 5 Approximate limits of areas of nickel- and copper-rich nodules in the subequatorial Pacific referred to in the text (productivity isolines in $gC m^{-2} y^{-1}$).

903W (**Figure 5**), is situated under the southern flank of the equatorial zone of high biological productivity on a seafloor composed of pelagic brown mud with variable amounts of siliceous and calcareous remains. Nodules from near the CCD at around 4250m are characterized by diagenetic growth and are enriched in Mn, Ni and Cu, whereas those from shallower depth are characterized mainly by hydrogenous growth. 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.

In the Tiki Basin there is also an increase in the Mn/Fe ratio of the nodules from south to north. All $Ni + Cu$ values are above the lower limit expected in diagenetically supplied material.

The Penrhyn Basin nodules fall compositionally within the lower and middle parts of the Mn/Fe range for Pacific nodules as a whole. However, nodules from the northern part of the Basin have the highest Mn/Fe ratios and highest Mn, Ni and Cu concentrations reflecting diagenetic supply of metals to them, although Ni and Cu decrease slightly as the equator is approached. 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 200 m above and below the CCD. The latititudinal variation in Mn, Ni and Cu in Penrhyn Basin nodules may be due to there being a hydrogenous source of these metals throughout the Basin, superimposed on which is a diagenetic source of them between about 2° and 6 $^{\circ}$ S at depths near the CCD, but less so in the very north of the Basin $(0-2^{\circ}S)$ where siliceous sedimentation prevails under highest productivity waters.

In the Nova Canton Trough area, manganese concentrations in the nodules are at a maximum 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 being centered just south of the equator at depths of $5300-5500$ m, just below the CCD.

In the central part of the Central Pacific Basin, between the Magellan Trough and the Nova Canton Trough, diagenetic nodules are found associated with siliceous ooze and clay sedimentation below the CCD. Their Ni and Cu contents increase southeastwards reaching a maximum at about $2.5^{\circ} - 3^{\circ}$ N and then decrease again towards the equator where productivity is highest.

The Clarion-Clipperton Zone deposits rest largely on slowly accumulated siliceous ooze and pelagic clay below the CCD. The axis of highest average Mn/Fe ratio and Mn, Ni and Cu concentrations runs roughly southwest-northeast with values of these elements decreasing both to the north and south as productivity declines respectively to the north and increases towards the equatorial maximum in the south.

Indian Ocean In the Indian Ocean, Mn-, Ni-, and Cu-rich nodules are present in the Central Indian Ocean Basin between about 5° and 15 \degree S. They are largely diagenetic in origin and rest on siliceous sediments below the CCD under high productivity waters. The deposits show north-south compositional variability with the highest grades occurring in the north.

Atlantic Ocean In the Atlantic Ocean, diagenetic Mn-, Ni-, and Cu-rich nodules occur most notably in the Angola Basin and to a lesser extent in the Cape/Agulhas Basin and the East Georgia Basin. These three areas have in common elevated biological productivity and elevated organic carbon contents in their sediments, which coupled with their depth near or below the CCD would help to explain the composition of their nodules. However, Ni and Cu contents are lower in them than in areas of diagenetic nodules in the Pacific and Indian Oceans.

Economic Potential

Interest in manganese nodules commenced around the mid-1960s and developed during the 1970s, at the same time as the Third United Nations Law of the Sea Conference. However, the outcome of that Conference, in 1982, was widely regarded as unfavorable for the mining industry. This, coupled with a general downturn in metal prices, resulted in a lessening of mining company interest in nodules. About this time, however, several governmentbacked consortia became interested in them and this work expanded as evaluation of the deposits by mining companies declined. Part 11 of the 1982 Law of the Sea Convention, that part dealing with deep-sea mining, was substantially amended in an agreement on 28 July 1994 which ameliorated some of the provisions relating to deep-sea mining. The Convention entered into force in November 1994.

During the 1980s interest in manganese nodules in exclusive economic zones (EEZs) started to increase. An important result of the Third Law of the Sea Conference, was the acceptance of a 200-nautical-mile EEZ in which the adjacent coastal state could claim any mineral deposits as their own. The nodules found in EEZs are similar to those found in adjacent parts of the International Seabed Area, and are of greatest economic potential in the EEZs of the South Pacific.

At the beginning of the twenty-first century, the out-look for manganese nodule mining remains rather unclear. It is likely to commence some time in this century, although it is not possible to give a precise estimate as to when. The year 2015 has been suggested as the earliest possible date for nodule mining outside of the EEZs. It is possible, however, that EEZ mining for nodules might commence earlier if conditions were favorable. It would depend upon many factors; economic, technological, and political.

Discussion

A model to explain the compositional variability of nodules in the Penrhyn Basin can be summarized as follows. Under the flanks of the high productivity area, reduced sedimentation rates near the CCD due to calcium carbonate dissolution enhance the content of metal-bearing organic carbon rich phases (fecal material, marine snow, etc.) in the sediments, the decay of which drives the diagenetic reactions that in turn promote the enrichment of Mn, Ni, and Cu in the nodules via the sediment interstitial waters. Away from the CCD, organic carbon concentrating processes are less effective. Further south as productivity declines, there is probably insufficient organic carbon supplied to the seafloor to promote the formation of diagenetic nodules at any depth. Under the equator, siliceous ooze replaces pelagic clay as the main sediment builder at and below the CCD, and when its rate of accumulation is high it dilutes the concentrations of organic carbon-bearing 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, although local factors may also apply. 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 reach a maximum south of the highest productivity waters. In the Tiki Basin, the greatest diagenetic influences are also found in the north of the Basin. As the South Pacific basins deepen to the west, the areas of diagenetic nodules tend to occur below the CCD as, for example, in the Nova Canton Trough area. This may be because the settling rates of large organic particles are quite fast in the deep ocean. Probably only limited decay of this material takes

place between it settling through the CCD and reaching the seafloor, and enough probably gets sedimented to extend the depth of diagenetic nodule formation to well below the CCD under high productivity waters where there is limited siliceous sediment accumulation.

In the North Pacific, the trends in nodule composition in relation to the equatorial zone are the mirror image of those in the south. 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 also has some applicability in the Indian Ocean but less in the Atlantic. In the Indian Ocean, diagenetic nodules associated with sediments containing moderate amounts of organic carbon occur resting on siliceous ooze to the south of the equatorial zone in the Central Indian Ocean Basin. Farther to the south these nodules give way to hydrogenous varieties resting on pelagic clay. However, in the north the changes in nodule composition that might be expected under higher productivity waters do not occur, probably because terrigenous sedimentation becomes important in those areas which in turn reduces the Mn, Ni, and Cu content of nodules. In the Atlantic, the influence of equatorial high productivity on nodule composition that is evident in the Pacific is not seen, mainly because the seafloor in the equatorial area is largely above the CCD. Where diagenetic nodules do occur, as in the Angola, Cape and East Georgia Basins, productivity is also elevated, but the seafloor is near or below the CCD leading to reduced sedimentation rates.

Conclusions

Manganese nodules, although not being mined today, are a considerable resource for the future. They consist of ferromanganese oxides variably enriched in Ni, Cu, and other metals. They generally accumulate around a nucleus and exhibit internal layering on both a macro- and microscale. Growth rates are generally slow. The most potentially economic varieties of the deposits occur in the subequatorial Pacific under the flanks of the equatorial zone of high biological productivity, at depths near the CCD. Similar nodules occur in the Indian Ocean under similar conditions.

See also

Authigenic Deposits. Hydrothermal Vent Fluids, Chemistry of. Hydrothermal Vent Biota. Hydrothermal Vent Ecology.

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De**nition**

The term mangrove is used to define both a group of plants and also a community or habitat type in the coastal zone. Mangrove plants live in or adjacent to the intertidal zone. Mangrove communities