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Deep-Sea Nodules and Co-rich Mn Crusts

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The mining of deep-sea manganese nodules has been a topic of interest since J.L. Mero undertook his preliminary studies in the 1960s to evaluate the prospects for mining deep-sea nodules. Despite the great deal of investment in deep-sea mining over more than 40 years, there has still been no successful attempt to mine the deep-sea nodules on a commercial scale. One of the major problems is that the nodules cannot be brought to the surface with the necessary amounts of recoverable nickel, cobalt and zinc to warrant the initial high investment necessary for this operation. It therefore appears that in the short term, deep-sea manganese and Co-rich Mn crusts will not be mined on a commercial scale in the foreseeable future. Nonetheless, investigations of deep-sea mineral deposits by a number of nations will continue and enable us to understand the deep-sea environment in increasing detail, which is necessary in view of the great extent of the deep oceans which cover an area of about 66% of the Earth’s surface.

Keywords: Co-rich Mn crusts, deep-sea manganese nodules, deep-sea mining, International Seabed Authority

Introduction

One of the greatest oceanographic expeditions of all time, the voyage of H.M.S. Challenger in which the Challenger circumnavigated the globe, took place from 1872 to 1876. During this expedition, large quantities of manganese nodules displaying a wide range of morphologies and internal structures were recovered from the Pacific, Indian and Atlantic Oceans. The highest abundances of nodules were recovered from the Pacific Ocean as a consequence of the huge size of the ocean and the resultant low average sedimentation rates. The findings of this expedition were to dominate the study of deep-sea manganese nodules until the 1960’s when systematic studies of deep-sea nodules and crusts began in earnest. The scientific results of this expedition were summarized by Murray and Renard (1891a) in their classic account of these deposits. Already, the expedition chemist, J.Y. Buchanan, had noted that the nodules were composed “of almost pure manganese peroxide” which is “one of the principal substances used in the manufacture of bleaching powder but which could never be made a paying source of supply.” Murray and Renard (1891b) were also the first to identify phillipsite in deep-sea nodules.

Deep-sea Nodules

Much attention has been directed to the study of deep-sea manganese nodules in the Pacific Ocean (Glasby 1970, 1976). It has been estimated that the oceans host about 10¹² t of nodules, making them a potential resource of economic interest. For example, the distribution of manganese nodules in the Pacific has been mapped as part of the Circum-Pacific Map Project using data from 2,500 bottom camera stations and from sediment cores (Piper et al. 1987) (Figure 1). However, commercial mining of nodules has still not taken place because of the great depth of the oceans, typically in the range 4,500–5,200 m, the difficulty of lifting these nodules to the surface at rates sufficient to make mining economically attractive and the rigors of working in a dynamic environment like the oceans which makes operating mining equipment at great depth over the side difficult, particularly in poor weather.

Main Types and Formation

There are three principal types of manganese nodules:

- Hydrogenetic nodules form by direct deposition of manganese and associated elements (cobalt, nickel and copper) from seawater at rates of about 1–2 mm Myr⁻¹. These nodules typically have Mn/Fe ratios of about one and relatively low concentrations of Mn, Fe, Cu, Ni and Co (Co + Ni + Cu concentrations of up to 3%).
- Diagenetic nodules are formed as a result of remobilization of manganese in the sediment column which results in nodules with enhanced Mn/Fe ratios and enhanced concentrations of Mn, Fe, Cu, Ni and Co.
Hydrothermal manganese deposits are formed as a result of the discharge of high temperature hydrothermal fluids at the seafloor (with temperatures up to 320°C). These high temperature fluids are typically found at hotspots and at divergent plate margins.

One of the main factors controlling the abundance of nodules on the sea floor is the sedimentation rate. In general, the highest concentrations of nodules occur on red clays or siliceous ooze where sedimentation rates are low, typically of the order of 1–3 mm/10^3 yr^-1 or less. However, high abundances of nodules also occur in regions where sedimentation is inhibited by strong bottom current scour, for example under the Antarctic Circum-Polar Current between Antarctica and Australia. The abundance of manganese nodules and crusts is also dependent on the length of time available for their accumulation. For example, traverses across both the Mid-Atlantic Ridge and the Carlsberg Ridge in the Indian Ocean show increasing thickness of these deposits with distance from the ridge crest (Glasby 1970). Nodules can also show considerable patchiness on the sea floor as a result of scour by ocean bottom currents around topographic highs and the availability of potential nucleating agents.

Hydrogenetic nodules are typically formed on red clay, which is characterized by very low rates of deposition, of the order of mm 10^3 yr^-1. The most extensive deposits of nodules are found in the deep-water regions of the Pacific and Indian Oceans in association with sharks’ teeth, whales’ ear bones, cosmic spherules and dark chocolate-coloured clays. One of the most extensive deposits of diagenetic manganese nodules in the World Ocean occurs between the Clarion and Clipperton Fractures Zones (C-C FZ) which is located between 6° 30’N and 20°N in the Equatorial North Pacific (von Stackelberg and Beiersdorf 1991). This area attracted considerable attention as a possible site for possible nodule mining in the 1960’s and 70’s, in part because of its proximity to Hawaii and the west coast of the United States (Margolis and Burns 1976).

Within the C-C FZ, there appear to be two discrete nodule types: larger “mature” nodules and smaller “immature” nodules. The nodules become flatter with increasing size and have a maximum diameter of 140 mm. These nodules are characterized by hydrogenous growth on the upper surface and diagenetic growth on the lower surface. Figure 2 shows the principal features of these hamburger nodules in this area. In addition, the morphology of the nodules is a function of the size class. Nodules <20 mm in diameter are dominantly fragments of larger nodules and less commonly discrete ellipsoidal nodules with botryoidal surface texture. Nodules in the 20–60 mm size classes are dominantly ellipsoidal to discoidal with the position of the sediment-water interface clearly defined. The upper surface of these nodules is mamillated with micro-botryoidal surface texture whereas the lower surface is less mamillated and smoother. Nodules in the >60 mm size class are dominantly highly mamillated and spheroidal with botryoidal surface texture on the upper

Fig. 1. Schematic map showing the distribution of manganese nodules in the Pacific Ocean. The contours represent the percentage of nodules on the ocean floor (adapted from Glasby 2000b).
Mineralogy

Mineralogically, manganese nodules consist of three principal phases; manganese oxides which tend to incorporate cationic transition metal species such as Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$, Fe oxyhydroxides which tend to incorporate anionic species such as HPO$_4^{2-}$, HAsO$_4^{2-}$, HVO$_4^{2-}$, MoO$_4^{2-}$ and WO$_4^{2-}$ as well as the Rare Earth Elements (REE), Co$^{3+}$ and detrital aluminosilicate minerals which consist of SiO$_2$, Al$_2$O$_3$, TiO$_2$ and Cr$_2$O$_3$. In addition, francolite (carbonate fluorapatite) occurs in the older generation of manganese crusts and as a discrete layer between the older and younger crust generations. The manganese oxide minerals are characterized by fine grain size in the range 100–1000 Å. These minerals are poorly crystalline and give diffuse X-ray diffraction patterns. There are three main manganese minerals in marine manganese deposits, 10 Å manganate, 7 Å manganate and $\delta$MnO$_2$, which are characterized by the following X-ray diffraction peaks:

<table>
<thead>
<tr>
<th>Phase</th>
<th>10 Å manganate</th>
<th>7 Å manganate</th>
<th>$\delta$MnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.7 Å 4.8 Å 2.4 Å 1.4 Å</td>
<td>7.3 Å 3.6 Å 2.4 Å 1.4 Å</td>
<td>2.4 Å 1.4 Å</td>
</tr>
<tr>
<td>(todorokite, buserite, 10 Å manganate)</td>
<td>(birnessite, 7 Å manganate)</td>
<td>(vernadite)</td>
<td></td>
</tr>
</tbody>
</table>

The mineralogy of manganese nodules is controlled by the redox conditions of the environment in which they formed. Shallow-water concretions from the Baltic Sea and Loch Fyne, Scotland, consist principally of 10 Å manganate, hydrothermal Mn crusts of 10 Å manganate and 7 Å manganate and deep-sea hydrogenous manganese nodules and crusts of $\delta$MnO$_2$. This trend is confirmed by the O/Mn ratios in nodules, which vary from 1.60 in shallow-water concretions to 1.95 in deep-sea nodules. Nearly all, 98%, of the manganese in deep-sea nodules is therefore in the form of Mn (IV). The pH$_{zpc}$ (pH of zero point of charge) is 1.5 for $\delta$MnO$_2$ and about 8 for hydrous iron oxides. As a result, elements such as Cu, Ni and Co (cationic species) are strongly adsorbed on deep-sea manganese nodules whereas Fe is present in nodules mainly in the form of FeOOH and adsorbs only limited amounts of other elements from seawater.

Burns and Burns (1978) have described the presence of authigenic todorokite and phillipsite in deep-sea manganese nodules based on observations by scanning electron microscopy and shown that these minerals line cavities and voids adjacent to areas where extensive leaching of biogenic siliceous debris has occurred within the nodules. In particular, clusters of todorokite crystallites containing Ni and Cu filling fissures, coating biogenic debris and infilling voids were observed where biogenic debris had once occurred in the

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Fig. 2. Hamburger-shaped nodule from the C-C FZ displaying a smooth surface texture on the upper surface and a rough surface texture on the lower surface (adapted from Glasby 2000b).

Fig. 3. Spherical nodule with cauliflower-shaped surface from the Peru Basin displaying rough surface texture on the upper surface and smooth surface texture on the lower surface (adapted from Glasby 2000b).
interiors of the nodules. According to these authors, post depositional growth of phillipisite and conversion of $\delta\text{MnO}_2$ to todorokite inside the nodules was promoted by the dissolution of biogenic siliceous debris.

**Co-rich Mn Crusts**

Co-rich Mn crusts may be defined as hydrogenous manganese crusts having a Co content $>1\%$. These crusts are typically 5–100 mm thick and occur on older seamounts (10–60 Ma) in the equatorial Pacific in the Mid-Pacific Mountains and Line Islands. The crusts are commonly found on exposed surfaces on the slopes of seamounts and on the summits of oceanic plateaux at water depths of 3000–1100 m. Principal substrates for the nodules include basalts, hyaloclastites, indurated phosphorite and claystone. On plateaux and flat terraces, manganese nodules can be seen lying on the surface of calcareous ooze. Ripple marks are sometimes observed in this ooze reflecting the presence of strong bottom currents. The average composition of crusts in the depth range 1500–1100 m in the Mid-Pacific Mountains is 28.4% Mn, 14.3% Fe, 0.50% Ni, 0.03% Cu and 0.5 ppm Pt with an average Mn/Fe ratio of 2.0. The principal manganese mineral present is $\delta\text{MnO}_2$ and the crusts have a growth rate of 1–2 mm $\times 10^{-3}$ yr$^{-1}$. Particularly noteworthy is the high concentration of Co in these crusts.

A very good summary of the data on deep-sea manganese deposits and Co-rich Mn crusts has been prepared by the International Seabed Authority (ISA, Technical Study: No. 11, 2013).

**Hydrothermal Mn Crusts**

Compared to manganese nodules and crusts, hydrothermal Mn crusts are relatively restricted in the marine environment and constitute less than 1% of the manganese deposits in the world’s oceans. These deposits occur in all types of active oceanic environments such as mid-ocean ridge spreading centres, back arc basins, island arcs and hot spot volcanoes.

As an example, hydrothermal Mn crusts from the Pitcairn Island hotspot in the eastern Pacific have been described in detail (Glasby et al. 1997) and their genesis can be explained by considering processes occurring within the hotspot volcano. Of key importance is the role of boiling of the ascending hydrothermal fluid, which leads to sulphide deposition and seawater intrusion into the upper part of the volcano. This in turn results in the development of an oxycline within the water column, above which FeOOH can precipitate. The high Mn/Fe ratios and low contents of Ni and Zn in the massive crusts reflect the rapid incorporation of the ore elements into the associated sulphide minerals such that only a small proportion of these elements are available for incorporation in the crusts themselves. The small positive Eu anomaly in the crusts is a result of the lower temperatures and the high Mn oxidation state in the hydrothermal fluids at the Pitcairn Island hotspot ($<25^\circ$C) compared to those at mid-ocean ridges ($c.$ 350°C).

Within this system, the oxyanions ($\text{CrO}_4^{2-}$, $\text{VO}_4^{3-}$, $\text{AsO}_4^{3-}$, and $\text{PO}_4^{3-}$), the rare earth elements (REE) and Th are scavenged by FeOOH particles within the upper part of the seamount and can therefore be incorporated into the crusts associated with the Fe-rich phase. Molybdenum and uranium, on the other hand, are scavenged in only negligible amounts by FeOOH. Molybdenum is therefore most probably scavenged from seawater by manganese oxides during the formation of the Mn crusts. The alkali metals, Li, Rb, and Cs, remain in solution in the hydrothermal fluids and are selectively incorporated into the buserite ($\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 21\text{H}_2\text{O}$) structure of the Mn crusts in the absence of strong competition from divalent transition metal ions.

The compositional characteristics of these hydrothermal Mn crusts can therefore be explained in terms of a simple model of element scavenging and uptake from hydrothermal fluids occurring mainly within the seamount. A laser-ablation Inductively coupled plasma mass spectrometry (ICPMS) profile in one of these crusts showed that the hydrothermal component was variable during the formation of the crust. It was calculated to be about 80% in the lower layers of this crust but almost 100% in the upper 18 mm of the crust.

Hydrothermal Mn crusts have also been located on Enarefa and Pulinuro seamounts in the Tyrrhenian Sea off the west coast of Italy (Eckhardt et al. 1997), along the Izu-Bonin-Mariana Arc (Usui et al. 1986, 1989; Usui and Nishimura 1992; Usui and Terashima 1997; Usui and Glasby 1998) and at the Pitcairn hotspot (Glasby et al. 1997; Scholten et al. 2004). The Tyrrhenian Sea is located near the African-European Fault. Within this area, there is a deep, narrow and distorted subduction zone, which is subducting away from the Ionian Sea towards the southern Tyrrhenian basin. This is a tectonically active zone favorable for the formation of hydrothermal fluids. The Tyrrhenian Sea crusts consist of porous, black, layered Mn oxides up to 45 mm thick. In some cases, the surface has a black metallic sheen. The crusts overlie substrates such as calcareous sediment, siltstone and oyster shells. A photograph of a hydrothermal Mn crust from the Tyrrhenian Sea is shown in Figure 4. The crusts consist dominantly of 10 A˚ manganate and 7 A˚ phosphate. Plagioclase and goethite. The sample having the highest Mn content contained 54.2% Mn, 0.07% Fe, 33 ppm Ni, 200 ppm Cu, 20 ppm Zn, 11 ppm Pb, and 910 ppm Ba with

**Fig. 4.** Upper surface of a hydrothermal crust from the Tyrrhenian Sea. Part of the upper surface displays the characteristic metallic sheen of hydrothermal manganese crusts (adapted from Glasby 2000b).
a Mn/Fe ratio of 774. It also had a low REE abundance and a negative Ce anomaly (Glasby et al. 2000b).

Hydrothermal Mn crusts are relatively rare in the oceans but offer an interesting insight into the occurrence and longevity of hydrothermal systems within the oceans. Rona (2008) has emphasized the role of plate tectonics in expanding our vision of marine minerals.

Deep-sea Mining

In principle, the occurrence of huge amount of manganese nodules (about 10^{12} t) containing significant amounts of Co, Ni, and Cu on the deep-sea floor and the presence of large amounts of Co-rich Mn crusts with high contents of Co and Pt on seamounts should make these deposits an attractive resource for deep-sea mining (Mero 1965, 1977; Glasby 2000a, 2007; Ren et al., 2007). However, even now, more than 40 years after the publication of John Mero’s influential book, The Mineral Resources of the Sea (Mero 1965), these deposits are still not being mined commercially.

As a result of a haul of nodules taken in shallow water about 370 km east of Tahiti during the International Geophysical Year in 1957–58, a study was undertaken by the University of California to determine whether it might be possible to mine and process manganese nodules for their Co, Ni, and Cu contents. Up to $250 million was spent over the following few years to evaluate the nodules as a potential resource and to develop mining and processing systems. Over 20 major mining companies took part in this exercise. The area chosen for the study was located between the Clarion and Clipperton Fracture Zones (C-C FZ) in the equatorial N Pacific at a water depth of about 4,500 m where rates of sedimentation are very low (1–2 mm/10^3 yrs) and are conducive to the formation of large nodules. The nodules become flatter with increasing size and have a maximum diameter of 14 cm.

To be minimally economic, the nodules need to be mined at a rate of about 5,000 t per day on a year-round basis. Using a 10 m wide gathering device, the nodule-collecting head would have to traverse the seafloor at a rate of 2 km/hr from a water depth of about 4,500 m and the nodules would need to have a Ni + Cu + Co content >2.5% to be economic. Ideally, the nodules would need to be mined at a rate of 3 Mt of nodules per year, equivalent to 8,200 tons/day, without a break throughout the year, not allowing for shutdowns for necessary maintenance work (Glasby 1983). This would be a formidable proposition. However, it should be borne in mind that manganese nodules are a relatively low-grade ore deposit located at great depth in a hostile environment (Hammond 1974a,b). Nonetheless, it should be borne in mind that mining deep-sea manganese nodules is based on the assumption that only 2.5–3.0% of the total mass of the nodules lifted from the deep-sea floor (\%Ni + Co + Cu) will be collected on the mining vessel for subsequent processing. This is a very low yield and explains why mining of deep-sea nodules has failed to become a major industry so far.

In order to mine nodules from the deep-sea floor on this scale, the nodules need to be brought to the surface by hydraulic lift in a riser pipe with a diameter 3 times that of the nodules in order to avoid clogging of the pipe which requires a minimum diameter of the pipe of 30–33 cm. It is the stringent requirements for lifting the nodules from the sea floor to the sea surface that has essentially prevented the development of a large-scale deep-sea mining industry.

Ferromanganese crusts, on the other hand, are typically found on hard-rock substrates at water depths less than 2,600 m and may cover up to 360 km² on a seamount. The distribution of these crusts on seamounts is complex and controlled by a wide-variety of factors including seafloor morphology, mass wasting, substrate rock type and age, subsidence history and ocean bottom current patterns. Mining these deposits is made difficult by the complex topography and structure of the deep seafloor and the variable distribution of the crusts on the seamounts. The development of this potential resource ultimately depends on the distribution of the crusts as well as on the small-scale topography, grade, and tonnage. In either case, the requirements for deep-sea mining are rigorous. As yet, there has been no commercial mining of deep-sea nodules or Co-rich Mn crusts. The basic problem is that deep-sea mining is not cost competitive with mining minerals on land.

The first attempt to exploit deep-sea manganese nodules ended in failure as a result of the collapse of world metal prices, the onerous provisions imposed by the U.N. Conference on the Law of the Sea (UNCLOS, 1982) and the overoptimistic assumptions about the viability of nodule mining (Glasby 2000a, 2002). Attention then focused on cobalt-rich manganese crusts from seamounts. Since the mid-1980s, a number of new players have committed themselves to long-term programs to establish the viability of mining deep-sea manganese nodules. However, these programs required heavy subsidy by host governments which has not been forthcoming. At present, there are some tentative plans, but none that are fully approved, to mine manganese nodules commercially.

In addition, seafloor massive sulphides (SMS) have attracted attention as a potential economic resource (Anon 2009). The first deep-sea hydrothermal vents to be discovered were located on the Galapagos Rift off Ecuador in 1977 (Corliss et al. 1979). These vents form above cracks in tectonically active areas where heated seawater with temperatures up to 400°C discharges on the seafloor. This creates a plume of black smoke on contact with seawater which results in the precipitation of sulphide minerals and the formation of “black smokers”. As a result, large chimneys of massive sulphides up to 20 m high form. These vents are found about every 100 km along the 65,000 km of the world’s mid-ocean ridges at water depths of 1–2 km and contain high concentrations of Cu, Au, Zn, and Ag. The deposits are surrounded by giant tubeworms that live on microbes that derive their energy not from photosynthesis but from the chemical compounds in the hydrothermal fluids. These deposits have the advantage of occurring within national Exclusive Economic Zones (EEZ) and can therefore be licensed by the host nation. In principle, it would be possible to mine
these deposits. However, there is already a glut of copper on the world market and there is no legal regime to cover mining of these deposits. For the moment, mining these deposits remains a prospect for the future.

There are also formidable engineering problems of working with large mining systems at depths of 4,500 m on the deep sea floor which are a major obstacle to deep-sea mining on a year-round basis. In our opinion, the Three-Million-Tons-Per-Year Manganese Nodule “Mine Site” which is equivalent to mining 8,219 t of nodules per day (or 5.7 t of nodules per minute) without a break throughout the year, is a very optimistic assumption which is unlikely to be achieved in practice using a single mining system. Hogland (1993) considered that the most optimistic date for the commercialization of deep-sea mining to be well into the 21st century. Given the fixed assumptions about technologies, there are many other reasons for being even more pessimistic about the commercial prospects for deep seabed mining.

There are two principal methods of mineral extraction for full-scale mining operations, the continuous-line bucket system (CLB) and the hydraulic suction system. The CLB system operates much like a conveyor-belt, running from the sea floor to the surface of the ocean where a ship or mining platform extracts the desired minerals and returns the tailings to the ocean. Hydraulic suction mining lowers a pipe to the seafloor which transfers nodules up to the mining ship. Another pipe from the ship to the seafloor returns the tailings to the area of the mining site. Recent technological advances have given rise to the use of remotely operated vehicles (ROVs) to collect mineral samples from prospective mine sites. Using drills and other cutting tools, the ROVs obtain samples to be analyzed for precious materials. Once a site has been located, a mining ship or station is set up to mine the area. However, these systems would not be appropriate for large-scale mining on the deep-sea floor.

In early 2011, Nautilus Minerals was granted a 20-year lease by the government of Papua New Guinea to mine at the Solwara Site 1 in the Manus Basin which will involve removing ores (and organisms) to a depth of 20–30 m on the seafloor. The company expects to begin open-cut mining there within the next few years covering an area equivalent to about 10 football fields (13,165 m²). In recent years, there are many other reasons for being even more pessimistic about the commercial prospects for deep-seabed mining.

In summary, deep-sea manganese nodules and Co-rich manganese crusts remain an important potential resource of selected elements for the late 21st century. Whether it will ever be possible to mine deep-sea manganese nodules on a competitive basis at the proposed rates of recovery without upsetting the ecological balance of the deep-oceans is another matter!

In short:

- There are about $10^{12}$ t of manganese nodules on the deep-sea floor.
- Diagenetic nodules contain high concentrations of Co, Ni and Co.
- However, these deposits are sub-economic at present.
- There are also extensive deposits of Co-rich Mn crusts on seamounts.
- Mining of Co-rich Mn crusts is made difficult by the complex topography and variable nature of the crusts on the seamounts.

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