

Manganese Nodules



1.1 The formation and occurrence of manganese nodules

Manganese nodules are mineral concretions made up of manganese and iron oxides. They can be as small as golf balls or as big as large potatoes. The nodules occur over extensive areas of the vast, sediment-covered, abyssal plains of the global ocean in water depths of 4 000 to 6 500 metres, where temperatures are just above freezing, pressures are high, and no sunlight reaches (Figure 2).

The manganese and iron minerals in these concretions precipitate (form a solid) from the ambient, or surrounding, water in two ways (Figure 3):

 hydrogenetically, in which the minerals precipitate from cold ambient seawater; and • diagenetically, in which minerals precipitate from sediment pore waters — that is, seawater that has been modified by chemical reactions within the sediment.

The metal oxides that make up the precipitate attach to a nucleus – perhaps something as small and common as a bit of shell or a shark's tooth – and very slowly build up around the nucleus in layers. Their mineralogy is simple: vernadite (a form of manganese oxide) precipitates from seawater; todorokite (another manganese oxide) precipitates from pore waters; and birnessite (a third manganese oxide) forms from the todorokite.

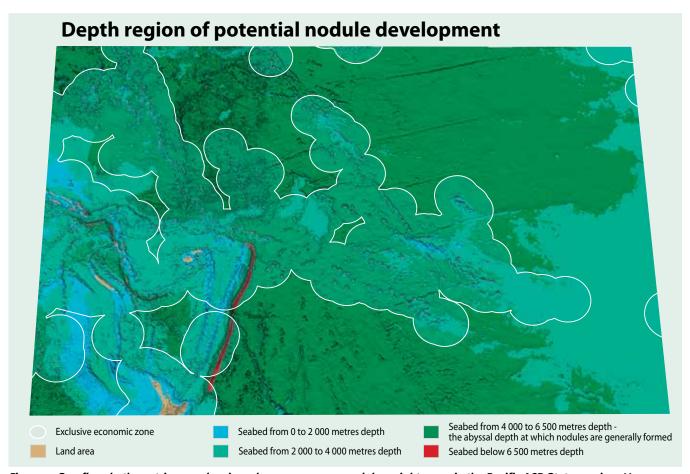


Figure 2. Sea-floor bathymetric map showing where manganese nodules might occur in the Pacific ACP States region. Manganese nodules occur at depths of 4 000 to 6 500 m, indicated by dark green in this map.

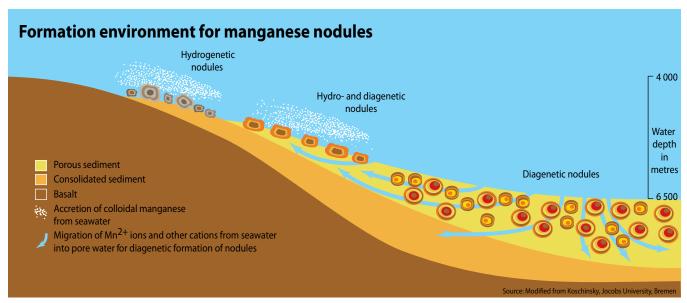
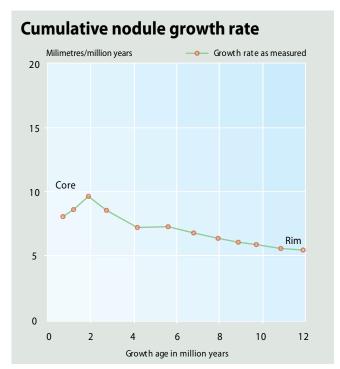


Figure 3. Formation of manganese nodules. This process takes place in water depths of 4 000 to 6 500 metres.

Hydrogenetic nodules grow extremely slowly, at a rate of about 1 to 10 mm per million years, while diagenetic nodules grow at rates of several hundred mm per million years. Most nodules form by both hydrogenetic and diagenetic precipitation and, therefore, grow at intermediate rates of several tens of mm per million years (Figure 4).



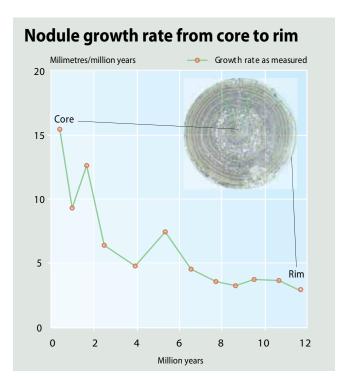


Figure 4. Growth age and growth rate of nodules. Growth age versus cumulative growth rate (left) and growth rate versus model age (right) in nodules from the Campbell Nodule Field, New Zealand. Extrapolated ages are based on measured 10Be/9Be ratios and the extrapolated 10Be/9Be ratio of the rim. Model ages are based on measured 10Be/9Be ratios and an assumed initial 10Be/9Be ratio. Growth ages (in m.y.) are based on the elapsed time from initiation of growth (i.e., core to rim). Graham et al. 2004.



of manganese nodules are revealed by the tree-ring-like texture of the nodule interior. Photo courtesy of Jim Hein, USGS.

The role of bacteria and organic matter in the formation of nodules is not well understood. The presence of bacteria could indicate a biological role in the formation of the nodules, but the bacteria could also be bystanders caught up in the process of mineralization. The very slow growth rates of nodules suggest that reactions linked with bacteria are not the major mechanisms of manganese and iron accretion. However, bacteria are the major players in sediment diagenesis, the process that releases manganese, nickel, copper, and lithium to the pore fluids, which then take part in forming the nodules (Hein and Koschinsky 2013). Bacterial activity and precipitation of organic matter may also play some role in the mineralization process.

The greatest concentrations of metal-rich nodules occur in the Clarion-Clipperton Zone (CCZ; ISA 2010, Figure 5), which extends from off the west coast of Mexico to as far west as Hawaii. Nodules are also concentrated in the Peru Basin, in the Penrhyn Basin near the Cook Islands (Figure 5), and at abyssal depths in the Indian and Atlantic oceans. In the CCZ, the man-

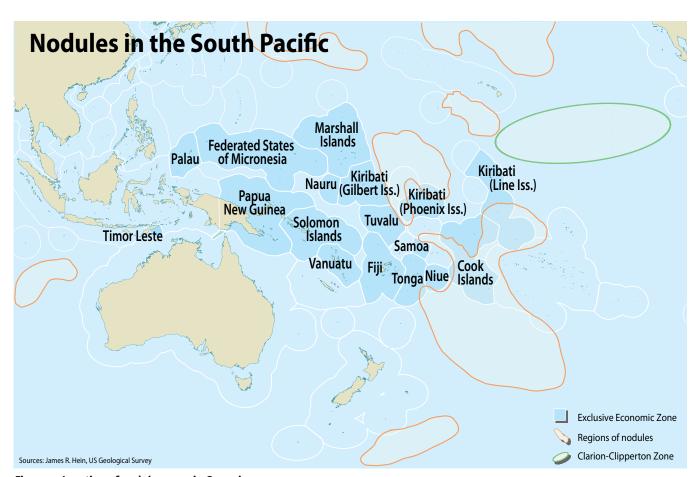


Figure 5. Location of nodule zones in Oceania.



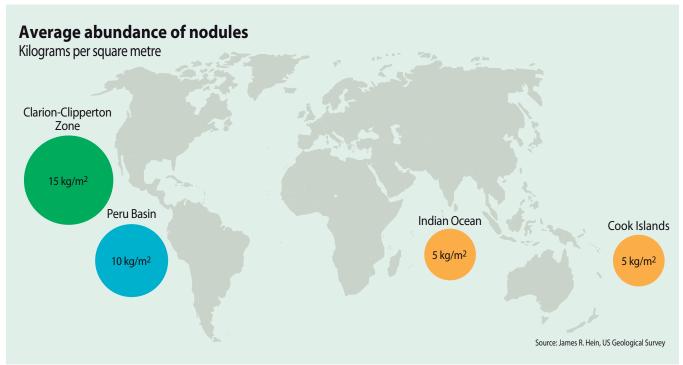


Figure 6. Current estimates of average nodule abundance in four major locations.

ganese nodules lie on abyssal sediments covering an area of at least 9 million square kilometres. Nodule densities can be as high as 75 kg per m2 of seabed within this area, but more commonly average less than 15 kg per m² (Figure 6).

The high abundance of nodules in the CCZ is attributed to a number of factors. The combination of slow rates of sedimentation and abundant sediment infauna (animals living within the sediment itself), which cause bioturbation and the uplifting of the nodules, helps to keep them on the surface of the seabed. The flow of Antarctic Bottom Water through the CCZ erodes and removes fine sediments, leaving abundant materials (such as fragments of broken nodules, mineral grains, and plankton shells) for the manganese and iron to nucleate around. This flow also keeps the bottom waters well oxygenated. The moderate surface-water productivity of the region provides the organic matter that the bacteria in the sediment use in diagenetic reactions, yet is not high enough to increase sedimentation rates. Finally, a semi-liquid bottom sediment layer provides abundant pore water to contribution to diagenetic nodule formation.



Physical characteristics of manganese nodules

Manganese nodules come in many shapes and sizes. They can be round, oblong, composite, or flat. Their shape can be influenced by the shape of the nucleus, the water content of the surrounding sediment, growth rates, and how often they are turned by infauna or moved by epifauna. As a general rule, smaller nodules tend to be more symmetrical. As nodules grow, they are less easily moved about by currents and animals, which leads to asymmetric growth resulting from faster diagenetic growth on the bottom and slower hydrogenetic growth on the top.

The surface texture of nodules depends partly on the dominant mechanism of formation. Other factors that influence texture include the size of the nodules, the strength of bottom currents, sediment on the surface of the nodules, and how often the nodules are turned (Figure 7). Diagenetic nodules tend to be rougher. Hydrogenetic nodules, in their most pure form, have a botryoidal surface (shaped like a bunch of grapes) that can be smooth or rough, but usually falls somewhere between those two extremes. If the surface is very smooth, it was likely worn down by bottom currents (Hein et al. 2000; Hayes et al. 1985).

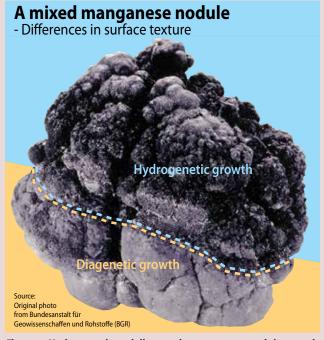


Figure 7. Hydrogenetic and diagenetic manganese nodule growth.

Metal concentrations and tonnages

Manganese and iron are the principal metals in manganese nodules (Figure 8). The metals of greatest economic interest, however, are nickel, copper, cobalt, and manganese. In addition, there are traces of other valuable metals - such as molybdenum, rare-earth elements, and lithium - that have industrial importance in many high-tech and green-tech applications and can be recovered as by-products (Figure 9).

The abundance of nodules and, therefore, the quantities of associated metals are moderately well known for the CCZ, the Central Indian Ocean Basin and the Cook Islands EEZ, but poorly known for other areas of the global ocean. A conservative calculation for the CCZ estimates there are about 21 100 million dry metric tonnes of nodules in the region. That would yield nearly 6 ooo million tonnes of manganese, more than the entire land-based reserve base of manganese (Hein and Koschinsky 2013). Similarly, the amount of nickel and cobalt in those nodules would be two and three times greater than the entire land-based nickel and cobalt reserve bases, respectively. The amount of copper in the CCZ nodules is about 20 per cent the size of the global land-based reserve base (Hein and Koschinsky 2013).

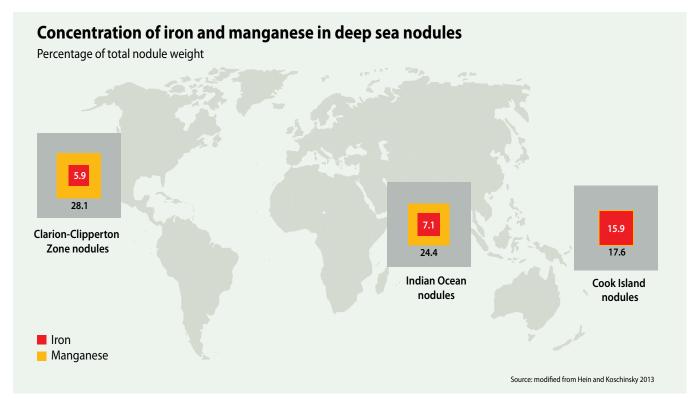


Figure 8. Varying percentages of iron and manganese in nodules from different environments. The iron/manganese ratio is controlled by the ratio of hydrogenetic/diagenetic input and whether or not the sediments involved in diagenesis are oxic, containing measurable amounts of oxygen. The Cook Islands nodules are almost solely hydrogenetic.

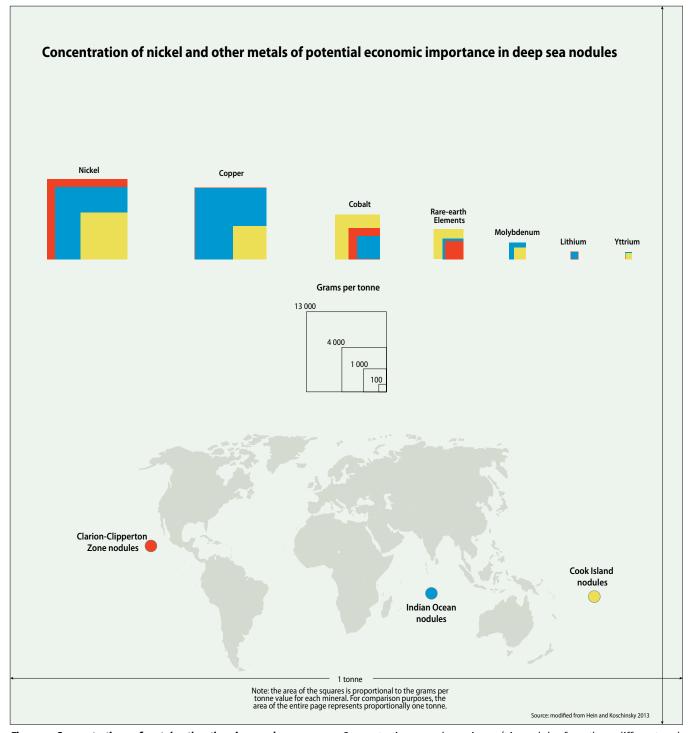


Figure 9. Concentrations of metals other than iron and manganese. Concentrations are shown in gm/t in nodules from three different nodule regions. For iron and manganese, see Figure 8.

Cook Islands manganese nodules

Characteristics of Cook Islands EEZ Nodule Resource

Water depth:	~5 000 m
Area of EEZ:	1 830 000 km² (see Fig. 1)
Area of nodules ≥5 kg/m2:	750 000 km²
Target metal:	Cobalt
Potential by products:	Nickel, copper, manganese, niobium, zirconium, rare-earth elements
Tonnage of nodules (dry):	5 130 000 000 tonnes
Cobalt grade:	0.41%
Tonnage of in-place cobalt:	21 033 000 tonnes
Global cobalt reserves (2012):	7 500 000 tonnes
Global cobalt reserve base (2009):	13 000 000 tonnes
Global cobalt production (2011):	98 ooo tonnes
Cobalt in 2x10 ⁶ dry tonnes nodules:	8 200 tonnes; ~8.4% of global production
Current cobalt price:	\$14-25/lb USD (\$31-55/kg)
35-years cobalt prices:	(see Figure 12)
Current profitable cobalt price:	≥\$25/lb
Projected cobalt price:	Steady for several years
Distance to Rarotonga:	Variable, <1160 km (from Manihiki)
Distance to processing plant:	~3 200 km (NZ) to ~5 700 km (Australia)

The parameters listed above, combined with average concentrations of 0.45 per cent for nickel, 0.23 per cent for copper, and 16 per cent for manganese, suggest in-place resources of 23 085 000 tonnes of nickel, 11 799 000 tonnes of copper, and 820 800 000 tonnes of manganese. These in-place tonnages are significantly greater than those that will be obtained after collection and processing of the nodules, since not all nodules in an area will be mined and some are lost in processing. Small areas (in the range of thousands of km²) with abundant (≥25 kg/m²), high-grade (~0.5 per cent cobalt) nodules will be the initial targets for mining operations, should such operations take place.

The Cook Island nodules are characterized by their high cobalt content (Figure 10 and Figure 11). Cobalt is becoming increasingly important, especially in the energy sector, due to its role in the production of rechargeable batteries. Cobalt is also used in a diverse range of industrial, hi-tech, medical, and military applications. The global cobalt market has historically

Cobalt, the target mineral for Cook Islands Average composition of the nodules Manganese 16% Nickel 0.45% **Cobalt 0.41%** Copper 0.23%

Figure 10. Current estimated average concentration of various metals in nodules from the Cook Islands. Data compiled by James R. Hein, USGS.

been very volatile (Figure 12). However, in recognition of the growing demand (Figure 13) and in an effort to provide greater price transparency, the London Minerals Exchange introduced cobalt futures trading at the beginning of 2010. Cobalt is traditionally produced as a by-product of the extraction of other metals, such as copper or nickel (Figure 14). The economic potential of the Cook Island nodules may increase if they are found to contain significant concentrations of rare metals and rare-earth elements. Determining this will require further geochemical analyses.

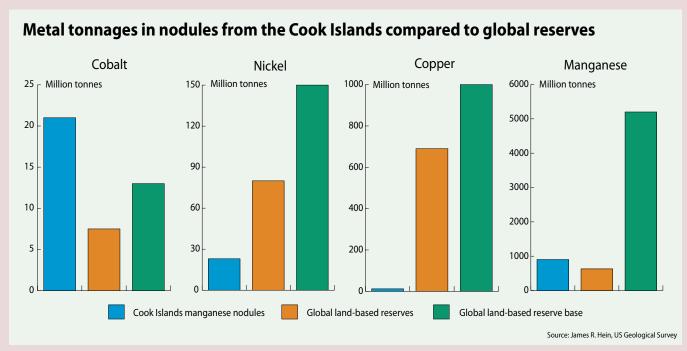


Figure 11. Current estimates of Cook Islands manganese nodules compared to global reserves. In-place tonnage of cobalt, nickel, copper, and manganese in Cook Islands nodules and a comparison with global land-based reserves and global land-based reserve base.

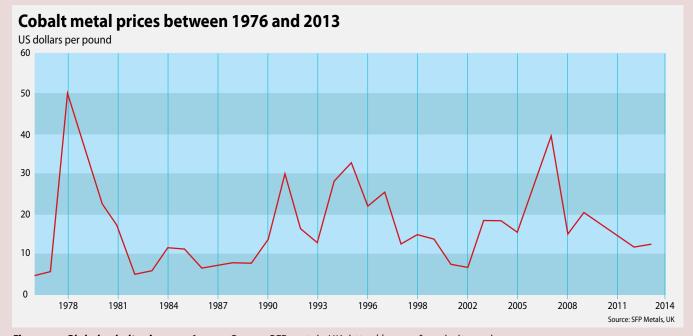


Figure 12. Global cobalt prices 1976-2011. Source SFP metals UK, http://www.sfp-cobalt.co.uk.

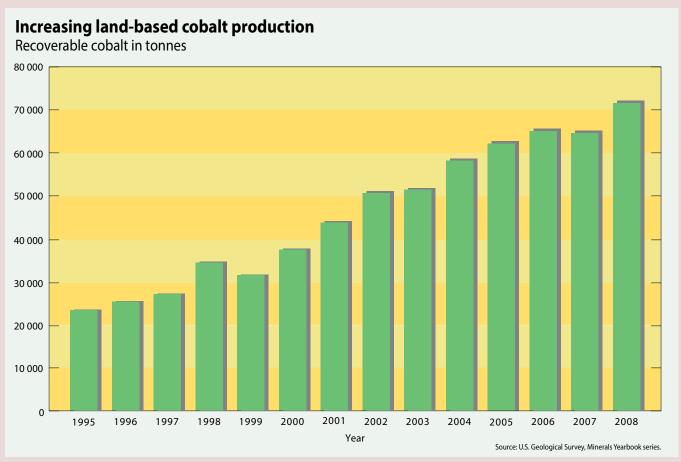


Figure 13. Increase in cobalt production. (Wilburn 2012).

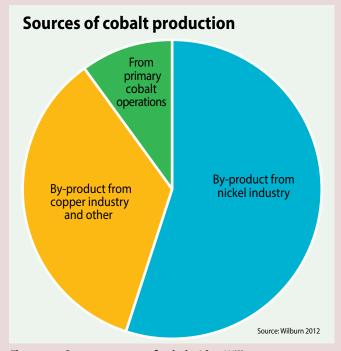


Figure 14. Current sources of cobalt. After Wilburn 2012.

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