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The Geology of Cobalt-rich Ferromanganese Crusts

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1.1 The formation and occurrence of cobalt-rich ferromanganese crusts

Cobalt-rich ferromanganese crusts precipitate onto nearly all rock surfaces in the deep ocean. Their thickness varies from less than 1 millimetre to about 260 millimetres. They occur only where the rock surfaces are free of sediment. There, they form pavements of intergrown manganese and iron oxides. Ferromanganese crusts may also coat rock pebbles and cobbles. They form at water depths of 600 to 7 000 metres on the flanks of seamounts (undersea mountains with a height above 1 000 metres), knolls (heights of 200 to 1 000 metres), ridges, and plateaus. Crusts with sufficient mineral content to be of economic interest commonly occur at depths of about 800 to

2 500 metres (Hein *et al.* 2000, 2009). In the Pacific Ocean, there are more than 11 000 seamounts (57 per cent of the global total) and 41 000 knolls (Yesson *et al.* 2011, estimated from the latest global bathymetry), and many more might exist in uncharted waters (Wessel *et al.* 2010). Many seamounts are within the Exclusive Economic Zones (EEZs) of Pacific Island states (Figure 2). The Atlantic Ocean has fewer seamounts, and the cobalt-rich crusts that occur there are usually associated with hydrothermal activity at sea-floor-spreading centres, with the exceptions of the northeast and northwest continental margin areas.

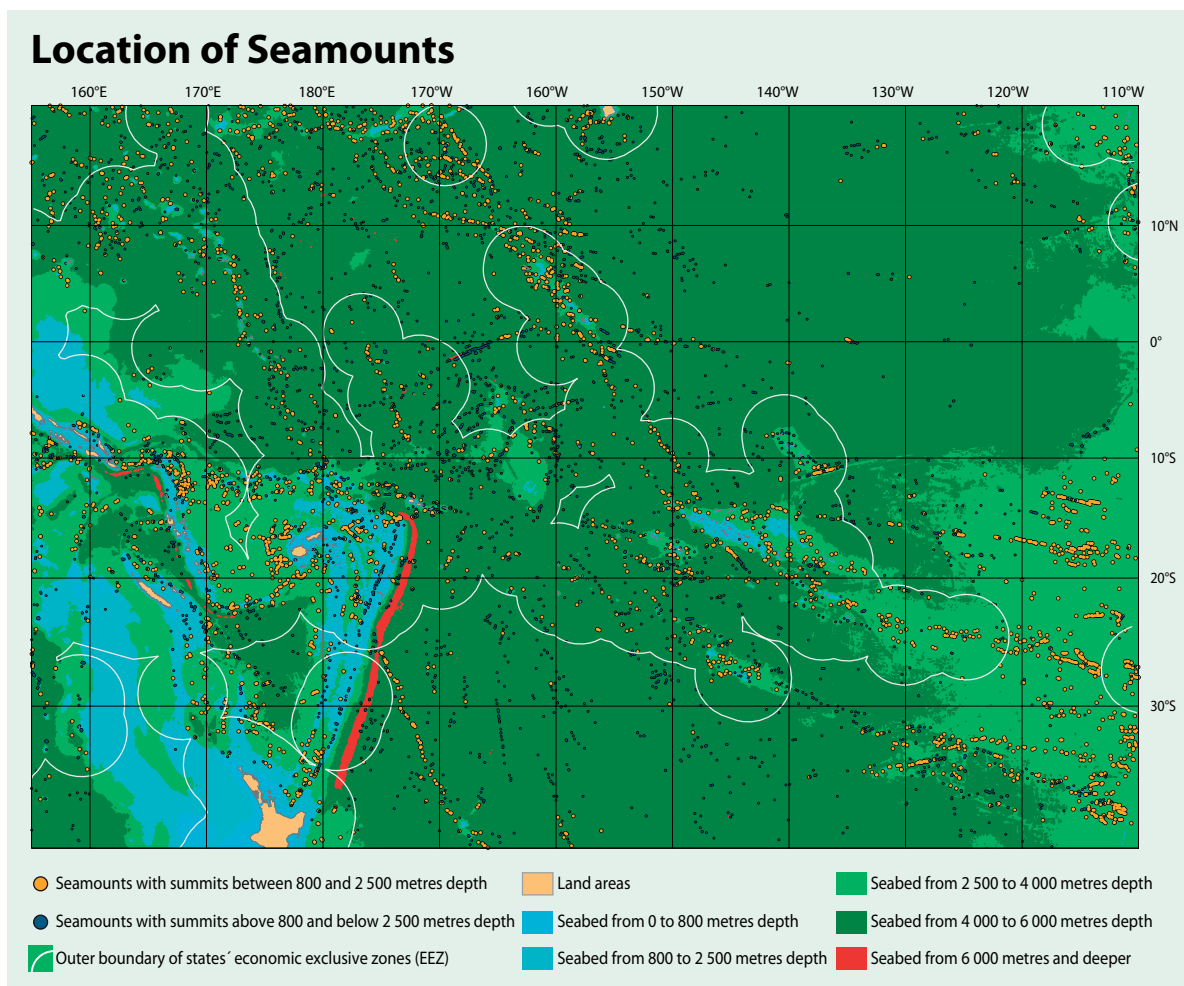


Figure 2. Bathymetric map of the Pacific showing the location of seamounts.

In the Pacific, the manganese and iron oxides precipitate out of cold ambient seawater (hydrogenetic) and are not associated with volcanic or hydrothermal activity (except at active volcanic arcs and hot-spot volcanoes). A wide array of metals and elements dissolved in ocean water are adsorbed (meaning to adhere to a surface) in large quantities onto the manganese and iron oxides (Figure 3). The main source of nearly all metals dissolved in seawater is erosion of the continents. The exception is manganese, which derives primarily from hydrothermal sources and mixes throughout the global ocean. The metals are adsorbed because of the crusts' very slow growth rates (1 to 5 millimetres per million years) and the enormous specific surface area (average 325 square metres per cubic centimetre of crust) (Hein *et al* 2000). The metals adsorbed include:

- trace metals, such as cobalt, nickel, and copper;
- rare metals, such as tellurium, platinum, zirconium, niobium, tungsten, and bismuth; and
- rare-earth elements, such as lanthanum, cerium, neodymium, europium, and terbium.

This makes ferromanganese crusts a potential resource for many of the metals used in emerging high-technology and green-technology applications.

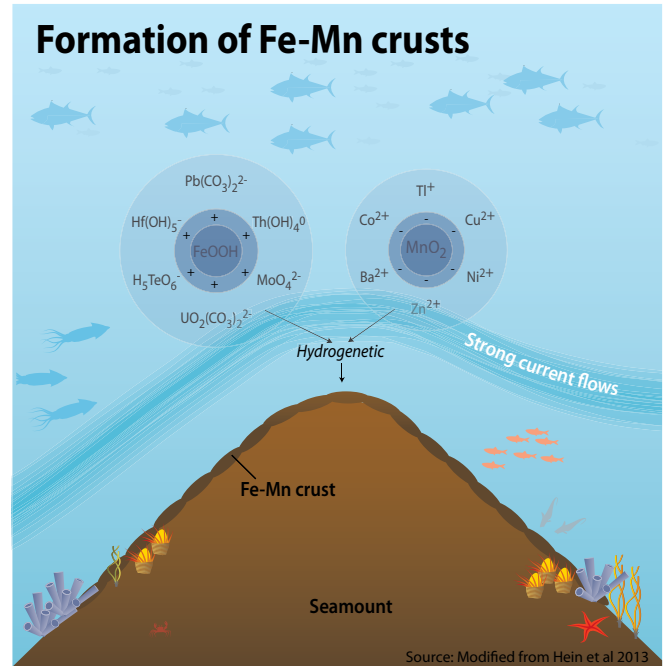
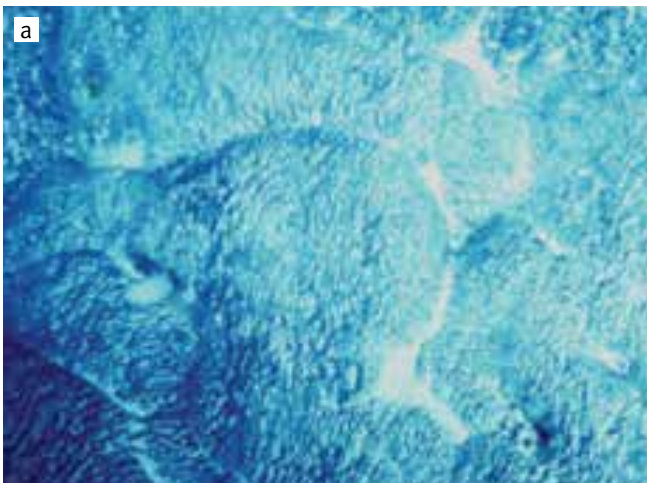


Figure 3. Formation of cobalt-rich ferromanganese crusts. Adapted from Hein 2004.



a: The seabed at 2 000 metres water depth showing ferromanganese crust pavement (~4 m by 3 m) on Horizon Guyot, Central Pacific. **b:** 18-cm-thick crust (D11-1) from 1 780 metres water depth within the Marshall Islands EEZ that started growing onto a substrate rock about 70 million years ago. **c:** A 12-cm-thick crust (CD29-2; cruise F7-86-HW) from the Johnston Island EEZ (USGS, Hein).

Hydrogenetic crusts, mixed hydrothermal-hydrogenetic crusts, and stratabound hydrothermal deposits

The crusts of economic interest are formed at the sea floor by precipitation from cold seawater (hydrogenetic), but iron and manganese oxides can also be created below the sea floor through hydrothermal processes. The hydrothermal deposits usually consist of stratabound layers of manganese, or iron, or manganese-cemented volcanoclastic and biogenic sediments. They are distinctly different in texture and composition from hydrogenetic ferromanganese crusts. The hydrogenetic crusts have similar amounts of iron and manganese, whereas the hydrothermal deposits are predominantly either iron or manganese (Hein *et al.* 2000). Hydrothermal activity dilutes the metals of economic interest, although small deposits can occasionally be enriched in lithium, molybdenum, chromium, zinc, nickel, or copper (Hein *et al.* 1997). At present, the economic potential of these hydrothermal deposits is uncertain, but might be reassessed with more investigation.

Farther away from the hydrothermal source, stratabound hydrothermal deposits grade into mixed hydrothermal-hydrogenetic crusts. These mixed-source crusts form at the seabed when the hydrothermal fluids exit the sea floor, mix with seawater, and precipitate onto hard rock surfaces. Those close to the hydrothermal source are very rich in iron and manganese but, like the stratabound deposits, have low concentrations of rare metals. As the distance from the source increases, the hydrothermal contribution wanes and the cold ambient seawater contribution dominates. Consequently, there is an increasing concentration of rare metals the farther away from the hydrothermal source the crusts are formed. The mixed hydrothermal-hydrogenetic crusts have no economic importance. Only the purely hydrogenetic (seawater source) crusts contain sufficient rare metals to be of current economic interest (Hein *et al.* 2000).



Ferromanganese crust on a boulder collected from the Ninety East Ridge, Indian Ocean. Photo courtesy of Evelyn Mervine.



Complex internal structure of ferromanganese crust. Photo courtesy of James R. Hein, USGS.

1.2 Metal concentrations and tonnage

Ferromanganese crusts have a simple mineralogy. They are composed predominantly of vernadite (manganese oxide, or MnO_2) and non-crystalline iron oxyhydroxide (FeOOH). This contrasts with manganese nodules, another type of deep sea mineral (see Volume 1B) containing similar metals, but having a more complex mineralogy – they are composed of two or three manganese minerals (vernadite, todorokite, and birnessite) in addition to non-crystalline FeOOH . Ferromanganese crusts also contain minor amounts of detrital minerals, such as quartz and feldspar. Most thick crusts (greater than about 60 millimetres) also contain a phosphate mineral called carbonate fluorapatite, which is a secondary mineral that forms long after the manganese and iron oxides have precipitated from seawater. Iron and manganese occur in approximately equal amounts in crusts (Figure 4). Cobalt,

the trace metal of greatest economic interest, can be up to 2 per cent, but usually averages 0.5 to 0.8 per cent by weight (Figure 5). Ferromanganese crusts contain the highest concentrations of the rare metal tellurium, which is used in the solar cell industry to produce thin-film photovoltaics – the best material for converting sunlight into electricity.

The concentration of metals other than iron and manganese in ferromanganese crusts is affected by the concentration of metals in seawater (the source), the Fe/Mn ratio of colloids in seawater and in crusts, and the surface charge of the Fe-Mn colloids. Cobalt and many other rare metals are adsorbed onto vernadite, which is more abundant in crusts than nodules, and this explains their generally higher concentrations in crusts (Hein

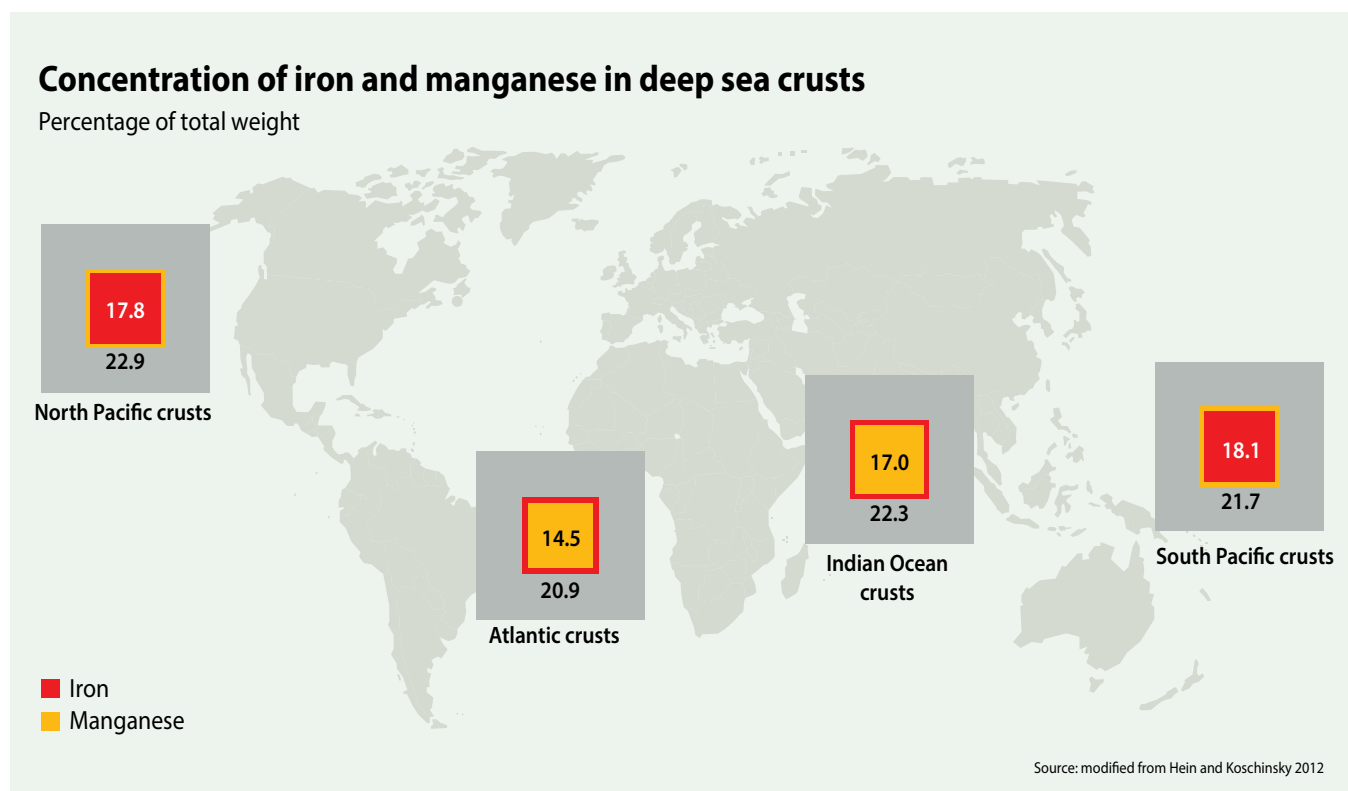
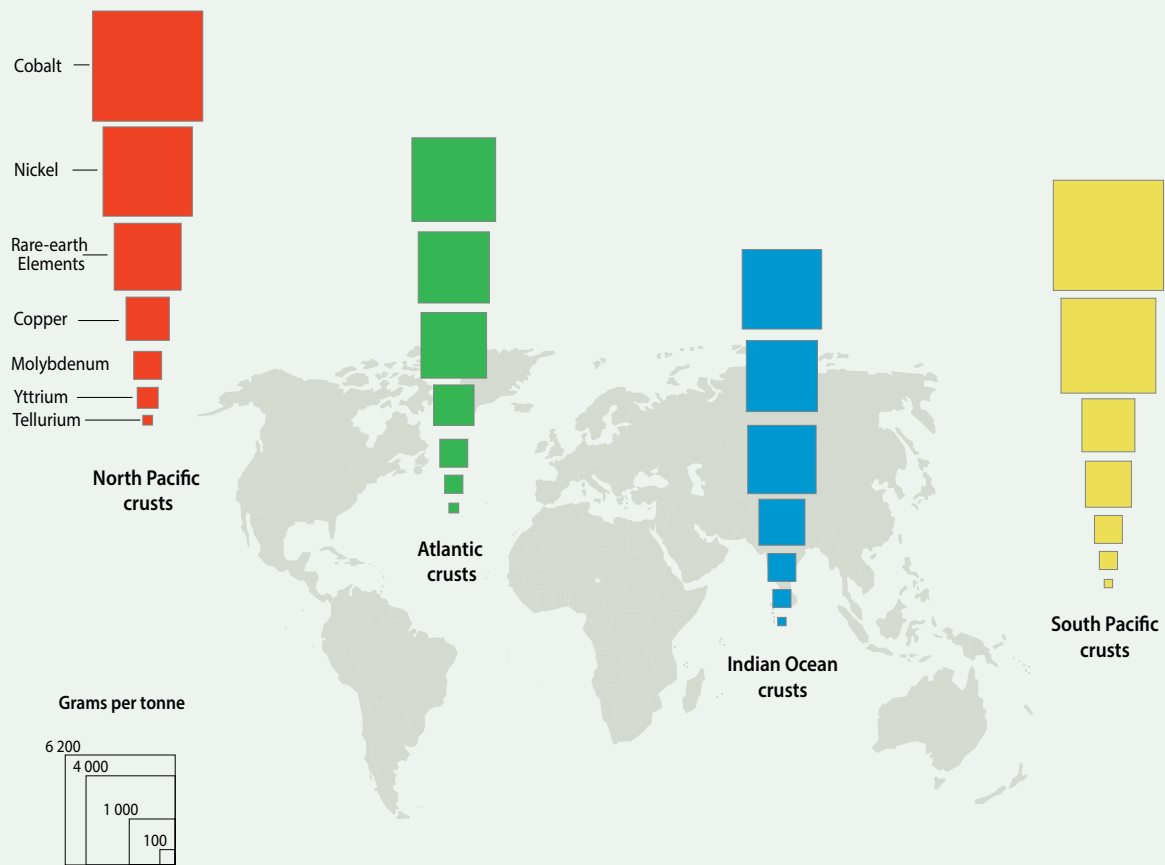


Figure 4. Concentration of iron and manganese in ferromanganese crusts.

Concentration of cobalt, nickel, and other metals of potential economic importance in ferromanganese crusts



Note: the area of the squares is proportional to the grams per tonne value for each mineral. For comparison purposes, the area of the entire page represents proportionally one tonne.

Source: modified from Hein and Koschinsky 2013

Figure 5. Concentration of metals of potential economic importance in ferromanganese crusts.



Ferromanganese crust on basalt substrate, collected during Monterey Bay Aquarium Research Institute (MBARI) cruise to the Taney Seamounts – a chain of four undersea volcanoes that lie about 300 kilometres due west of Monterey Bay, California – from August 5–13, 2010 (see <http://www.mbari.org/expeditions/Taney10>)

and Koschinsky 2013). The rare metals tellurium and platinum are also more highly concentrated in crusts than nodules because they are sorbed onto the iron oxyhydroxide phase, which is more abundant in crusts.

Little is known about the abundance of ferromanganese crusts in most areas of the global ocean. The thickest crusts with the highest concentrations of cobalt have been found on outer-rim terraces and on broad saddles on the summits of seamounts (Hein *et al* 2008). The central equatorial Pacific region – particularly the EEZs around Johnston Island and Hawaii (United States), the Marshall Islands, the northern part of the Federated States of

Micronesia, and international waters of the mid-Pacific – is currently considered the most promising area for crust mining. A rough estimate of the quantity of crusts in the central Pacific region is about 7 533 million dry tonnes (Hein and Koschinsky 2013).

Ferromanganese crusts on seamounts in the central Pacific are estimated to contain about four times more cobalt, three and a half times more yttrium, and nine times more tellurium than the entire land-based reserve base of these metals. These crusts also contain the equivalent of half of the bismuth and a third of the manganese that makes up the entire known land reserve base (Hein and Koschinsky 2013).

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