

Study to investigate state of knowledge of deep sea mining

Final report Annex 1 Geological Analysis

FWC MARE/2012/06 – SC E1/2013/04

Client: DG Maritime Affairs and Fisheries

Rotterdam/Brussels,

15 October 2014



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Table of contents

List of abbreviations	5
Summary	7
1 Overview	9
1.1 Aim	9
1.2 Results	9
2 Seafloor Massive Sulphides	11
2.1 The formation and occurrence of seafloor massive sulphides	11
2.2 Metal concentrations and tonnages	13
2.3 Factors controlling geochemistry	16
2.3.1 Tectonic Setting	16
2.3.2 Size and shape of seafloor massive sulphides deposits	17
3 Manganese nodules	20
3.1 The formation and occurrence of manganese nodules	20
3.2 Metal concentrations and tonnages	22
4 Ferromanganese crusts	25
4.1 The formation and occurrence of manganese nodules	25
5 Recommendations for areas of future work on marine mineral resources	29
6 References	32

List of abbreviations

Au	Gold
Bi	Bismuth
CCZ	Clarion-Clipperton Zone
Cd	Cadmium
Co	Cobalt
Cu	Copper
EEZ	Exclusive Economic Zones
Ga	Gallium
Ge	Germanium
In	Indium
ISA	International Seabed Authority
Mn	Manganese
MOR	Mid-ocean ridge
MORB	Mid-ocean ridge basalt
Mt	Million tons
ODP	Ocean Drilling Program
Pb	Lead
PB	Peru Basin
PEN	Penrhyn Basin
PZ	Prime Zone
Sb	Antimony
SMS	Seafloor massive sulphides
Te	Tellurium
Ti	Thallium
Zn	Zinc
Zr	Zirconium

Summary

Polymetallic sulphides (also known as seafloor massive sulphides – SMS) are occurrences of metal-bearing minerals that form on and below the seabed as a consequence of the interaction of seawater with a heat source (magma) in the sub-seafloor region of volcanic ridges and along volcanic arcs. They are typically found on and around mid-ocean and back arc ridges where they are formed in the process of tectonic movements. The total number of such vent sites that exists on the modern sea floor is not known, although several hypotheses have been used to infer their abundance.

Based on our review, we assess that the size of an individual sea floor massive sulphide deposit varies from a few tonnes to >15 million tons (Mt) of ore material. However, reliable size estimates are very rare since drilling information is needed to accurately infer the tonnage of polymetallic sulphide occurrences. This information is only present for very few sites. For most occurrences information on their size relies on visual estimates of the surface area that is covered by hydrothermal precipitates. Most of the explored polymetallic seafloor sulphide occurrences are small¹. The exceptions to this are the brine pool deposits in the Red Sea, including the Atlantis II Deep deposit, which is by far the largest known metal deposit (90 Mt) on the modern seafloor².

Polymetallic nodules occur widely on the vast, sediment-covered plains of the abyssal ocean at depths of about 4 000 to 6 500 m. They are mineral concretions made up of manganese and iron oxides that can be found in sizes as small as golf balls or as big as large potatoes. The greatest concentrations of metal-rich nodules occur in the Clarion-Clipperton Zone (CCZ), which extends from off the west coast of Mexico to as far west as Hawaii. Nodules are also concentrated in the Peru Basin, near the Cook Islands, and at abyssal depths in the Indian and Atlantic oceans.

Manganese and iron are the principal metals in polymetallic nodules. The metals of greatest economic interest, however, are nickel, copper, cobalt, and possibly manganese if this can be extracted and processed in a commercially viable manner. In addition, there are traces of other valuable metals, such as molybdenum, rare-earth elements (REE), and lithium that have industrial importance in many high-tech and green-tech applications and can possibly be recovered as by-products once appropriate extraction and processing techniques have been developed.

Cobalt-rich **polymetallic crusts** precipitate onto nearly all rock surfaces in the deep ocean that are free of sediment. Here, they form pavements of manganese and iron oxides. Polymetallic crusts may also coat rock pebbles and cobbles. Their thickness varies from less than 1 millimetre to about 260 millimetres. They form at water depths of 600 to 7 000 m on the flanks of volcanic seamounts, ridges, and plateaus.

Many seamounts are within the Exclusive Economic Zones (EEZs) of Pacific Island states. The Atlantic Ocean has fewer seamounts. Cobalt-rich polymetallic crusts are often associated with hydrothermal activity at seafloor-spreading centres, with the exceptions of the northeast and northwest continental margin areas. Cobalt is one of the trace metals of greatest economic interest and commonly shows values greater than 0.5 weight % Cobalt. Another metal of great interest is

¹ Less than one million tonnes

² We distinguish between modern and ancient seafloor. Copper, zinc, lead, silver, and gold are often mined from ancient black smoker deposits (co-called VMS deposits) that were transferred from the ancient seafloor onto land through geological processes (obduction). They occur in various countries e.g. Spain and Portugal, Russia and Cyprus or Germany.

Tellurium (Te), which globally averages about 50 ppm (parts per million) in crusts, with a maximum value found of 205 ppm³.

Comparison of characteristics and resource potential of deep-sea marine mineral resources. REE = Rare earth elements; CCZ = Clarion-Clipperton Zone; PCZ = Prime Crust Zone (Hein et al., 2013)

	Sulphides	Mn nodules	Co-rich crusts
Geological setting	mid-ocean ridges and young island arc volcanoes	sedimented abyssal plains	flanks of old volcanoes
Characteristics	ten to several hundred meter wide mounds	baseball-sized nodules on soft sediment	several cm thick crusts paving hard substrate
Water depth of greatest economic potential	1,000 – 5,000 m	3,000 – 6,000 m	1,000 – 2,500 m
Distribution	3-dimensional	2-dimensional	2-dimensional
Main metals of interest	Copper Zinc, Gold, Silver	Manganese, Copper, Nickel, Cobalt	Manganese, Copper, Nickel, Cobalt
Other metals considered	Cadmium, Gallium, Germanium, Indium, Antimony	Molybdenum, Lithium, Zirconium	Rare Earth Elements, Tellurium, Platinum
Resource estimate	600 million tonnes estimated to occur in the neovolcanic zone of mid-ocean ridges	21,100 million tonnes in the CCZ	7,533 million tonnes in PCZ
Grades	(global average) 5 wt.% Copper; 10 wt.% Zinc; 5 ppm Gold; 200 ppm Silver	(CCZ) 28 wt.% Manganese; 2.4 wt. % Nickel plus Copper; 0.2 wt.% Cobalt	(PCZ) 23 wt.% Manganese; 0.5 wt. % Nickel plus Copper; 0.7 wt.% Cobalt; 0.2 wt.% REE
Grade distribution	heterogeneous on local scale	homogeneous within large regions	homogeneous within large regions
Knowledge base for resource estimate	poor	good	moderate
Resource potential of the commodity	medium	high	high
Global impact of mining on metal markets	low	high	high
Size of the mining area	small	large	large

³ Hein et al., 2013

1 Overview

1.1 Aim

The aim of the geological analysis is to establish an overview of the location, formation processes, grades and tonnages, and geological controls of deep-sea marine mineral deposits. These include manganese nodules occurring on the seabed of the abyssal plains, cobalt-rich ferromanganese crusts that are associated with the flanks of old volcanic seamounts, and massive sulphides that form in volcanically active areas along mid-ocean ridges and at submarine volcanoes related to subduction zones.

1.2 Results

Site-specific Information on Marine Mineral Resources

The project team used publicly available data on individual samples and sites for all three deep-sea mineral deposits. For sample specific information on manganese nodules (2753 samples) and ferromanganese crusts (1224 samples) we used the compilation of the International Seabed Authority (ISA Central Data Repository). For massive sulphide occurrences the InterRidge vents database version 2.1 was used⁴ that covers discoveries up to 2010 and we updated this with published recent information covering new findings after 2010.

Since the InterRidge database contains numerous entries of low-temperature hydrothermal emanations that are not proven to be of economic interest, we used only those sites that have indications of sulphides present in their descriptions (306 sulphide occurrences with a total number of 5103 individual chemical analyses).

Table A.1.1.1 Comparison of characteristics and resource potential of deep-sea marine mineral resources. REE = Rare earth elements; CCZ = Clarion-Clipperton Zone; PCZ = Prime Crust Zone (Hein et al., 2013)

	Sulphides	Mn nodules	Co-rich crusts
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⁴ Beaulieu, S.E., Baker, E.T., German, C.R., Maffei, A. (2013): An authoritative global database for active submarine hydrothermal vent fields. *Geochem. Geophys. Geosyst.* 14, 4892–4905.

	Sulphides	Mn nodules	Co-rich crusts
	5 ppm Gold; 200 ppm Silver	Copper; 0.2 wt.% Cobalt	Copper; 0.7 wt.% Cobalt; 0.2 wt.% REE
Grade distribution	heterogeneous on local scale	homogeneous within large regions	homogeneous within large regions
Knowledge base for resource estimate	poor	good	moderate
Resource potential of the commodity	medium	high	high
Global impact of mining on metal markets	low	high	high

2 Seafloor Massive Sulphides

2.1 The formation and occurrence of seafloor massive sulphides

Sea-floor massive sulphides are occurrences of metal-bearing minerals that form on and below the seabed as a consequence of the interaction of seawater with a heat source (magma) in the sub-seafloor region⁵ of volcanic ridges and along volcanic arcs (Fig. A.1.3.1). During this process, cold seawater penetrates through cracks in the sea floor, reaching depths of several kilometres below the sea-floor surface, and is heated to temperatures above 400°C. The heated seawater leaches out metals from the surrounding rock. The chemical reactions that take place in this process result in a fluid that is hot, slightly acidic, reduced, and enriched in dissolved metals and sulphur. Due to the lower density of this evolved seawater, it rises rapidly to the sea floor, where most of it is expelled into the overlying water column as focused flow at chimney vent sites. The dissolved metals precipitate when the fluid mixes with cold seawater. Much of the metal is transported in the hydrothermal plume and is deposited as fallout of particulate debris. The remainder of the metal precipitates as metal sulphides and sulphates, producing black and white smoker chimneys and mounds.

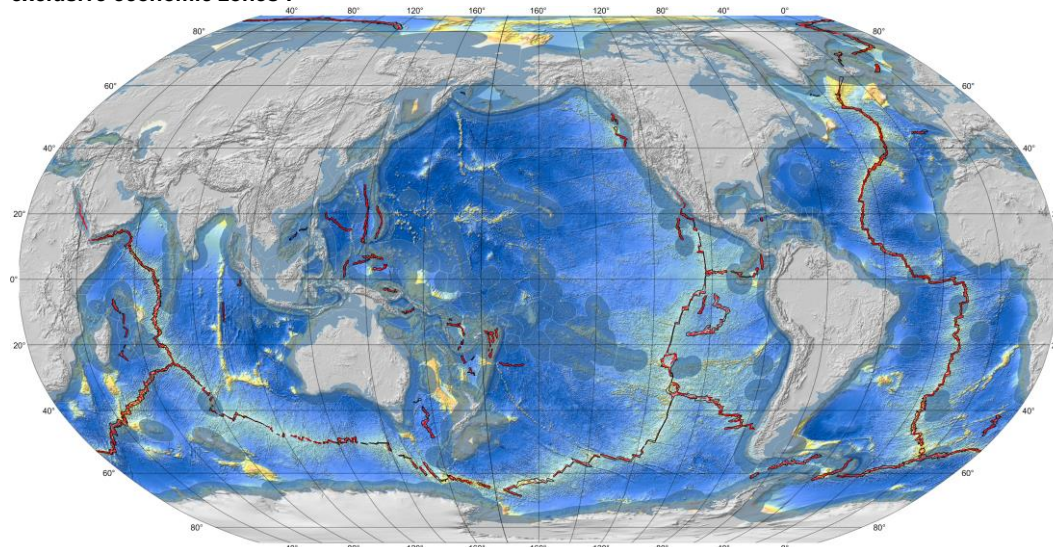
The minerals forming the chimneys and sulphide mounds include iron sulphides, such as pyrite, as well as the main minerals of economic interest such as chalcopyrite (copper sulphide) and sphalerite (zinc sulphide). The precious metals gold and silver also occur, together with non-sulphide (gangue) minerals, which are predominantly sulphates and silicates. The metals originate from immiscible sulphides, ferromagnesian silicates, and feldspars that make up the volcanic rocks beneath the seafloor⁶. It has been suggested that rising magmatic fluids may also be a source of ore metals, particularly at sites where hydrothermal systems are producing seafloor massive sulphides deposits in close association with subduction zones and island arcs. The enriched magmatic fluid would then mix with the circulating seawater⁷.

⁵ Hannington, M.D., de Ronde, C.D., Petersen, S. (2005). Sea-floor tectonics and submarine hydrothermal systems. *Economic Geology 100th Anniversary Volume* 111–141.

⁶ Ibid.

⁷ Yang, K., Scott, S.D. (1996): Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. *Nature* 383, 420–423; Yang, K., Scott, S.D. (2002): Magmatic degassing of volatiles and ore metals into a hydrothermal system on the modern sea floor of the eastern Manus back-arc basin, western Pacific. *Economic Geology* 97, 1079–1100.

Figure A.1.2.1 Mid-ocean and back-arc ridges important for the formation of seafloor massive sulphides. The areas shown here contain the rift valleys (black) and axial ridges (red) that were defined from global morphological features identified by GRID Arendal⁸. Bluish grey areas near coastlines are world exclusive economic zones⁹.



Since black smokers were first discovered, more than 300 sulphide occurrences have been identified in all oceans (this report), indicating that hydrothermal convection is widespread (Fig. A.1.3.2). Most sulphide occurrences (65 %) have been found along mid-ocean ridges, with another 22 % occurring in back-arc basins and 12 % along submarine volcanic arcs. Very few sites (1 %) have been observed at intraplate volcanoes.

Spreading centres (mid-ocean ridges and back-arc basins) have a combined length of 67,000 kilometres¹⁰, whereas submarine volcanic arcs have a total length of 22,000 kilometres¹¹. At mid-ocean ridges, high-temperature venting occurs mainly in the axial zones of the spreading centres and is associated with basaltic volcanism. At slow-spreading ridges, however, long-lived detachment faults may divert fluid flow away from the ridge axis. The associated sulphide deposits can, therefore, be found several kilometres away from the ridge axis. Currently the occurrence farthest away from the ridge axis is the St. Petersburg site at the Mid-Atlantic Ridge¹², which is located 16 km west of the axis. Volcanic arcs and back-arc basins develop as a result of subduction of oceanic crust at a convergent plate boundary. Hydrothermal systems in these environments are broadly similar to those at mid-ocean ridges. However, the geology and tectonic setting influence the composition of the hydrothermal fluids and also, ultimately, the mineralogy and chemical composition of the associated sulphide deposits. The apparent differences are related to variations in host-rock composition, as well as to direct input of magmatic volatiles and metals into the hydrothermal circulation cell¹³. The occurrence and distribution of sulphide deposits seems to be related to overall magmatic activity along plate boundaries.

⁸ Harris, P.T., Macmillan-Lawler, M., Rupp, J., Baker, E.K. (2014): Geomorphology of the oceans. *Marine Geology* 352, 4–24.

⁹ VLIZ vers 8, 2014; www.marineregions.org

¹⁰ Bird, P., (2003): An updated digital model of plate boundaries. *Geochem. Geophys. Geosyst.* 4, 10.1029–2001GC000252.

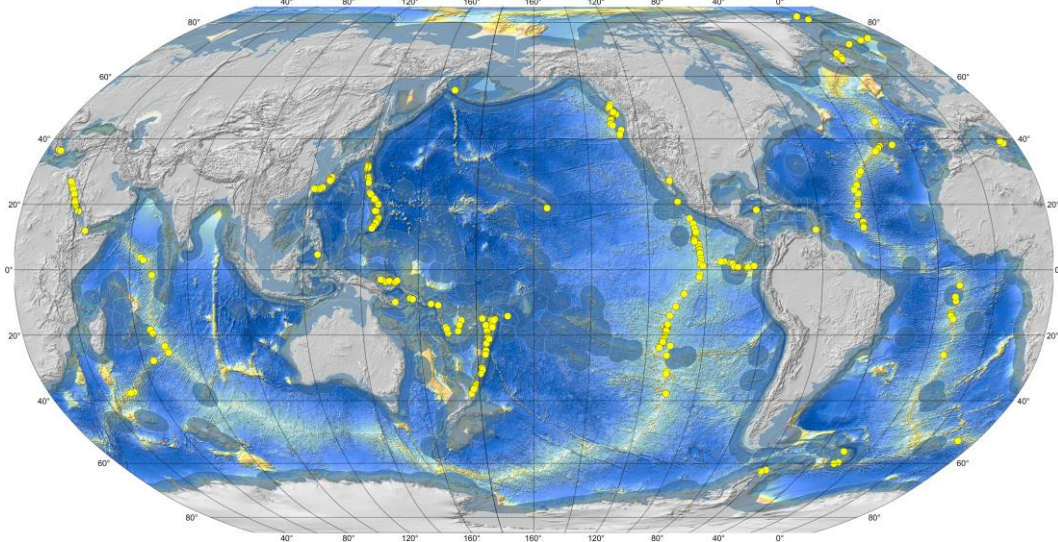
¹¹ de Ronde, C.E., Faure, K., Bray, C.J., Chappell, D.A., Wright, I.C. (2003): Hydrothermal fluids associated with seafloor mineralization at two southern Kermadec arc volcanoes, offshore New Zealand. *Mineralium Deposita* 38, 217–233.

¹² Cherkashev, G.A., Ivanov, V.N., Bel'tenev, V., Lazareva, L.I., Rozhdestvenskaya, I.I., Samovarov, M.L., Poroshina, I.M., Sergeev, M.B., Stepanova, T.V., Dobretsova, I.G., Kuznetsov, V.Y. (2013): Massive sulfide ores of the northern equatorial Mid-Atlantic Ridge. *Oceanology* 53, 607–619.

¹³ Yang, K., Scott, S.D. (1996): Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. *Nature* 383, 420–423; de Ronde, C.E.J., Massoth, G.J., Butterfield, D.A., Christenson, B.W., Ishibashi, J., Ditchburn, R.G., Hannington, M.D., Brathwaite, R.L., Lupton, J.E., Kamenetsky, V.S., Graham, I.J., Zellmer, G.F., Dziak, R.P., Embley, R.W.,

The total number of vent sites that exist on the modern sea floor is not known, although several hypotheses have been used to infer their abundance. Estimates based on Earth's heat flow indicate that approximately one black smoker per kilometre of ridge axis is necessary to explain the heat flux through the oceanic crust¹⁴. The distribution of hydrothermal plumes along the spreading axis and over volcanic arcs has also been used to infer similar values. It should be noted, however, that the latter approach only considers active hydrothermal fields. Evidence suggests that there are many more inactive sites than active sites¹⁵.

Figure A.1.2.2 Location of seafloor massive sulphide occurrences investigated for this report (306 sites).



2.2 Metal concentrations and tonnages

While the number of discoveries of seafloor massive sulphides occurrences is steadily rising, most deposits are small in size and tonnage of contained sulphide. Hydrothermal vent systems do not generally incorporate metals into sulphide deposits efficiently. Much of the metal is lost to the hydrothermal plume and dispersed away from the vent sites. Large deposits form only where sediments allow for efficient trapping of the metals due to metal-precipitation below the sea floor (as in Middle Valley and Okinawa Trough)¹⁶ or where hydrothermal activity occurs for long periods of time, as with sulphide mineralization related to large detachment faults. Based on information about the age of the sulphides and the underlying volcanic crust, it appears that tens of thousands of years are needed to form the largest known deposits.

Dekov, V.M., Munnik, F., Lahr, J., Evans, L.J., Takai, K. (2011). Submarine hydrothermal activity and gold-rich mineralization at Brothers Volcano, Kermadec Arc, New Zealand. *Mineralium Deposita* 46, 541–584.

¹⁴ Mottl, M.J. (2003) Partitioning of energy and mass fluxes between mid-ocean ridge axes and flanks at high and low temperature, in: Halbach, P.E., et al., eds., *Energy and mass transfer in marine hydrothermal systems: Dahlem Workshop Report 89*: Berlin, Dahlem University Press, p. 271–286.

¹⁵ Hannington, M., Jamieson, J., Monecke, T., Petersen, S., Beaulieu, S. (2011): The abundance of seafloor massive sulfide deposits. *Geology* 39, 1155–1158.

¹⁶ Zierenberg, R.A., Fouquet, Y., Miller, D.J., Bahr, J.M., Baker, P.A., Bjerkgård, T., Brunner, C.A., Duckworth, R.C., Gable, R., Gieskes, J., Goodfellow, W.D., Gröschel-Becker, H.M., Guerin, G., Ishibashi, J., Iturrino, G.J., James, R.H., Lackschewitz, K.S., Marquez, L.L., Nehlig, P., Peter, J.M., Rigsby, C.A., Schultheiss, P., Shanks, W.C., III, Simoneit, B.R.T., Summit, M., Teagle, D.A.H., Urdat, M., Zuffa, G.G. (1998): The deep structure of a sea-floor hydrothermal deposit. *Nature* 392, 485–488; Takai, K., Mottl, M.J., Nielsen, S.H.H., the IODP Expedition 331 Scientists (2012): IODP Expedition 331: Strong and Expansive Subseafloor Hydrothermal Activities in the Okinawa Trough. *Scientific Drilling* 13, 19–27

The composition of SMS deposits is highly variable, and not all elements contained in the sulphides are of commercial interest. For example, SMS deposits along the East Pacific Rise and, to some extent, those along the Mid-Atlantic Ridge are primarily composed of iron sulphides (Tab. A1.3.1) that currently have no economic value¹⁷. In contrast, sulphide occurrences in the southwest Pacific contain concentrations of copper (Cu) and zinc (Zn), which make them more economically attractive. Valuable metals such as gold and silver are trace components of the sulphides but can be highly enriched in some deposits, reaching concentrations of several tens of grams/tonne for gold and several hundreds of grimes/tonne for silver (Tab. A.1.3.2). Other trace elements such as antimony (Sb), bismuth (Bi), cadmium (Cd), gallium (Ga), germanium (Ge), indium (In), tellurium (Te), and thallium (Tl), are normally contained in SMS in low quantities (at levels measured in grimes/tonne), but can be significantly enriched in some deposits, especially those that form at volcanic arcs (Tab. A.1.3.2). Weathering of old SMS on the seabed can upgrade the metal contents in the deposit due to the formation of secondary copper-rich sulphides.

The geochemical composition of seafloor massive sulphides is not only variable on a regional scale, but also varies at the deposit or even hand-specimen scale, reflecting strong gradients in fluid temperatures. Copper-rich minerals typically line the high-temperature upflow zones and fluid conduits. The outer parts of the deposits consist of minerals that are rich in iron and zinc, such as pyrite, marcasite, and sphalerite. These are usually deposited at lower temperatures as the hydrothermal fluid mixes with seawater.

As a result of this heterogeneity, the sampling of black smoker chimneys, which commonly show high concentrations of copper, might not be representative of the bulk composition of the deposits. Many published grades of sea-floor sulphide deposits are strongly biased due to sampling of high-temperature chimneys, which are easier to recover than sub-sea-floor mineralization. Unfortunately, with the exception of a few deposits that have been drilled through the Ocean Drilling Program or by commercial or scientific projects, little is known about the interiors of most seafloor massive sulphides deposits. **Due to lack of information about the important subsurface component of deposits, it is difficult to estimate the resource potential of most seafloor massive sulphides.** Initial estimates of the abundance and distribution of sulphide deposits in well-studied areas indicate that approximately 1,000 large sulphide deposits may exist on the modern sea-floor¹⁸.

However, some of the largest deposits, such as those along the central Mid-Atlantic Ridge, are dominated by iron sulphides of no commercial interest – according to the current state of knowledge. Other factors that affect current commercial viability are water depth, distance to land, and sovereign jurisdiction. An analysis of the 306 known deposits, notwithstanding the limited information on the grade and the lack of data from the interior of the occurrences, allows the speculation that probably no more than ten individual deposits may have sufficient size and grade to be considered for future mining¹⁹. So far, only the Atlantis II Deep and Solwara 1 have sufficient grade and tonnage to be of interest, however, smaller, metal-rich deposits could be incorporated into a single mining operation, making mining of these smaller SMS deposits viable.

¹⁷ Hannington, M.D., de Ronde, C.D., Petersen, S. (2005). Sea-floor tectonics and submarine hydrothermal systems. *Economic Geology 100th Anniversary Volume* 111–141

¹⁸ Hannington, M., Jamieson, J., Monecke, T., Petersen, S., Beaulieu, S. (2011): The abundance of seafloor massive sulfide deposits. *Geology* 39, 1155–1158.

¹⁹ Ibid

Table A.1.2.1 The mean metal content of seafloor massive sulphides with respect to their tectonic setting (source GEOMAR) Note that the trace metals gold, silver and arsenic are in parts per million (ppm)

Setting	N	Cu %	Zn %	Pb %	Fe %	Au ppm	Ag ppm	As ppm
sediment-free MOR	2302	4.9	8.0	0.2	26.9	1.2	93	365
ultramafic-hosted MOR	556	13.6	9.8	0.1	27.0	8.5	84	212
sediment-hosted MOR	173	1.1	3.6	0.5	24.7	0.5	84	1692
intraoceanic back arc	898	3.5	15.7	0.7	13.5	6.1	226	885
transitional back-arcs	789	5.6	18.4	1.5	7.1	12.0	312	10573
intracontinental rifted arc	136	3.3	19.0	9.7	7.1	5.3	916	4950
volcanic arcs	178	3.8	12.7	2.0	9.8	12.6	328	2010

From the known vent sites geochemical data is only available for 130 occurrences. However, as stated above, a number of these occurrences contain few metals of economic interest. Since most deposits have only been sampled at the surface we used thresholds of 5 wt.% Cu, 15 wt.% Zn and 5 grams/tonne gold (Au) to indicate a base (Cu, Zn) or precious metal potential for the occurrences. Based on these criteria, 82 occurrences show enrichments of one or more of these metals (Fig. A.1.3.3). It needs to be emphasized that geochemistry is not the only important parameter; size does matter (see below). A number of other elements may occur in large quantities in single samples, however, on a regional scale these elements do not seem to be economically important (Tab. A.1.3.2). Certain deposits may contain sufficient concentrations of one or more of these elements to improve economic viability, however, sufficient data is currently lacking to prove the case.

Figure A.1.2.3 Location of seafloor massive sulphide occurrences with base and/or precious metal enrichment (source GEOMAR; N=82).

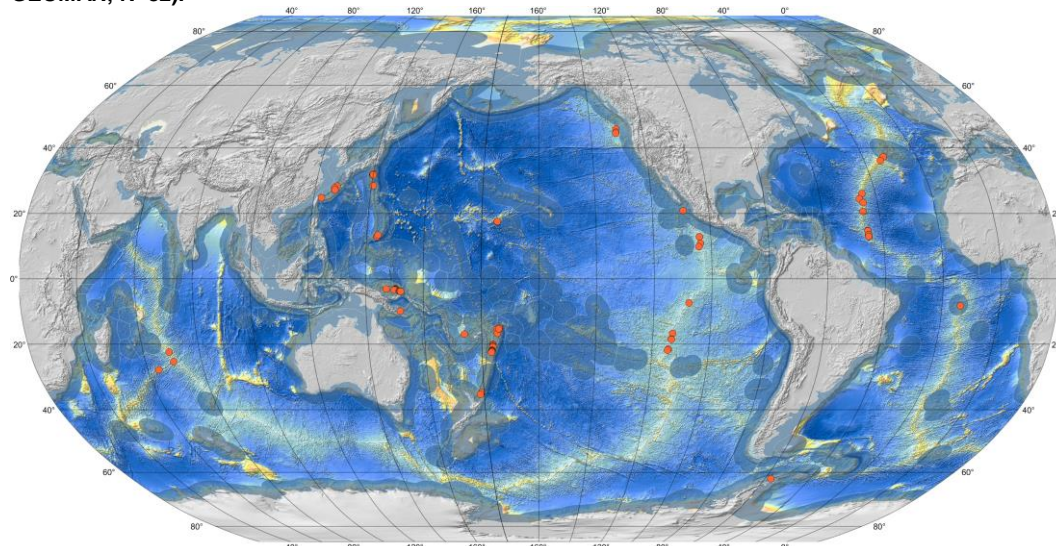


Table A.1.2.2 Range and mean concentration of selected trace metals present in SMS occurrences (source GEOMAR). Note that these elements are not routinely measured for seafloor massive sulphides and therefore the number of analyses is much lower than those for base and precious metals.

Element	N	range (ppm)	mean (ppm)
antimony	2468	<1 – 40,200	310
bismuth	958	<1 – 2,000	17
cadmium	2508	<1 – 6,300	370

Element	N	range (ppm)	mean (ppm)
gallium	728	<1 – 1,870	38
germanium	583	<1 - 918	26
mercury	1542	<1 – 6,400	42
indium	827	<1 - 592	18
selenium	2041	<1 – 9,700	128
tellurium	695	<1 - 230	5
thallium	694	<1 – 1,440	35

2.3 Factors controlling geochemistry

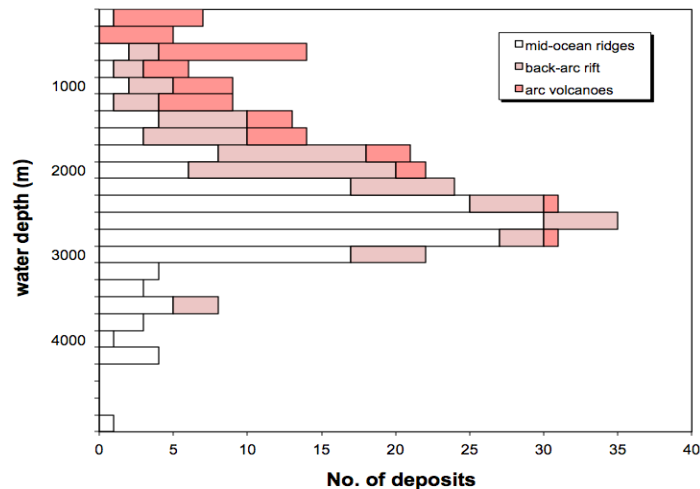
2.3.1 Tectonic Setting

The composition and hence the metal-content of the source rock influenced by the hydrothermal circulation is closely connected to the tectonic setting. At mid-ocean ridges, the composition of the source rock is relatively homogenous “MORB” (mid-ocean ridge basalt). MORBs are divided into N-MORB (“normal”) and E-MORB (“enriched”). These values refer to the amount of incompatible/compatible elements in the host rock. The presence of enriched MORB influences the concentration of, for instance, Ba in the ores. Another difference that is known to influence the metal contents and grades of massive sulphides on the sea floor is the amount of sediment cover on top of the MORBs. In general, ridges with sediment cover are large (efficient trapping of metal-bearing fluids), have lower than average metal-grades, higher Zn and lead (Pb) than sites on unsedimented ridges. This is due to the metal-content being diluted by abundant non-ore material. However, sediments and or volcanoclastics create an efficient cap for hydrothermal fluids therefore helping in forming large occurrences.

At volcanic arcs and back-arcs, especially of the western Pacific, the source rock is more variable than at MORs. This variation is directly reflected in the composition of the massive sulphides, which are often higher in copper and gold grade. Here, the subducting slab, a piece of old-seafloor composed of volcanic and magmatic rocks and sediment, influences the systems at arcs and back-arcs. Additionally, in such a tectonic setting metals are interpreted to be enriched via direct magmatic input of metals and volatiles into the hydrothermal system.

Water depth is often closely tied to the tectonic setting (Fig. A.1.3.4) and also an important factor influencing the exploitability and metallogeny of seafloor massive sulphide deposits. The majority of mid-ocean ridge (MOR) sites are distributed at 2-3 km depth, whereas arc sites are generally situated at shallower water depths. Back-arc rifts are found at a wide variety of water depths. Water depth (pressure) influences the boiling temperature of hydrothermal fluids and thus the metallogeny of the deposits. Deposits situated at great water depth are difficult and expensive to exploit, but deposits that occur at shallow water depths (< 1000 meter) are characterized by low confining pressure that causes the mineralizing fluids to boil before reaching the seafloor. This boiling causes precipitation of the metals of interest below the seafloor and results therefore in lower metal grades in the deposit at the seafloor. This is especially true for copper and such deposits will have less economic interest.

Figure A.1.2.4 Depth distribution of occurrences investigated for this progress report (N=290). Majority of mid-ocean ridge (MOR) sites are distributed at 2-3 km depth, whereas arc sites are generally situated at shallower water depths. Back-arc rifts are found at a wide variety of water depths. Water depth (pressure) influences the boiling temperature of hydrothermal fluids and thus the metallogeny of the deposits.



2.3.2 Size and shape of seafloor massive sulphides deposits

Based on our review, the size of a seafloor massive sulphide deposit varies from a few tonnes to > 15 Mt of ore material, however, reliable size estimates are very rare since drilling information is needed to accurately infer the tonnage of massive sulphide occurrences. This information is only present for very few sites (Table A.1.3.3; Fig. A.1.3.5). For most occurrences information on their size relies on visual estimates of the surface area that is covered by hydrothermal precipitates. By far most seafloor sulphide occurrences are small! The exceptions to this are the brine pool deposits in the Red Sea, including the Atlantis II Deep, by far the largest metal deposit (90 Mt) on the modern seafloor. Here, the ore material is deposited as unconsolidated metal-bearing muds instead of massive sulphide²⁰.

The main styles of deposits are sulphate and sulphide chimneys and mounds. Individual chimneys can vary in size from only a few centimetres to up to 45m. It is important to note, that up to 90% of the metals carried by the fluids through chimneys is eventually lost to seawater where it is dispersed as a plume. Chimneys collapse with time and create sulphide accumulation at the site of hydrothermal activity (talus) that can form a substantial part of a sulphide deposit. Chimney formation may be focused, forming larger structures, or distributed over larger area, for example along a fissure, thereby often forming smaller chimneys. Sulphate and sulphide mounds may also grow by inflation as more material is accumulated to the core of the mound. Such mounds are often zoned, with the surface being more Cu- and Zn-rich than the core (e.g., TAG, Middle Valley, PacManus, Palinuro which have all been drilled). This information is vital for any global or site-specific resource estimates that are based on surface samples only. Those results will likely not be representative for the deposits as a whole. Sub-seafloor accumulations such as those at Middle Valley on the Juan de Fuca Ridge, where massive sulphide accumulations occur beneath a sediment cover and much less is known about this type of deposit growth on the modern ocean floor. In these systems hot fluids do not vent to the seafloor, instead cooling and precipitation is confined to the pore space of sediments or volcanoclastics. Such systems are difficult to find but clearly more efficient in retaining the metal sulphides within proximity to the vent site and they have

²⁰ Nawab, Z.A. (1984): Red Sea mining: a new era. Deep Sea Research Part A. Oceanographic Research Papers 31, 813–822.

the potential to form very large deposits. Many volcanic massive sulphide deposits mined on land are inferred to have formed in this type of “sealed” environment.

Reliable estimates of the total sulphide accumulation in submarine sulphide deposits are only possible in a few cases where drilling has provided information on deposit thickness. Drilling results from the large TAG mound, which measures 200 m in diameter and 45 m in height, indicate 2.7 million tonnes of massive sulphide averaging 2 % Cu plus 1.2 million tonnes of stockwork at 1% Cu. During Ocean Drilling Program (ODP) Leg 139, drilling at Middle Valley, on the Juan de Fuca Ridge, intersected massive sulphide accumulations and subsequent drilling of the Bent Hill and ODP mounds at Middle Valley during Leg 169 confirmed a total tonnage of between 10 and 15 million tonnes. Data from extensive commercial drilling of the Solwara 1 deposit near Papua New Guinea has been used to estimate a deposit size of 2.3 Mt. Current mining scenarios are working with an annual tonnage of sulphide ore of approx. 2 million tonnes. There are only few deposits of this size known from the modern seafloor, but some have been found in most of the settings where seafloor hydrothermal activity occurs, including the mid-ocean ridges (Galapagos, TAG, Alvin Zone, Krasnov, and Semyenov sites), sedimented ridges (Middle Valley), intraoceanic back-arc basins (North Fiji Basin), volcanic arcs (Myojin Knoll), and rifted arcs in transitional or epicontinental environments (JADE, Solwara 1). However, only few deposits in the largest size class (top 10%) are thought to exceed 2 million tonnes in size. It should be noted that the size estimates for many of the supposedly large deposits along the Mid-Atlantic Ridge are not based on drilling results. For our purpose of defining economically interesting deposits those with accumulations of less than 1 million tonnes are considered small.

Table A.1.2.3 Seafloor sulphide occurrences for which size information is available based on drilling information.

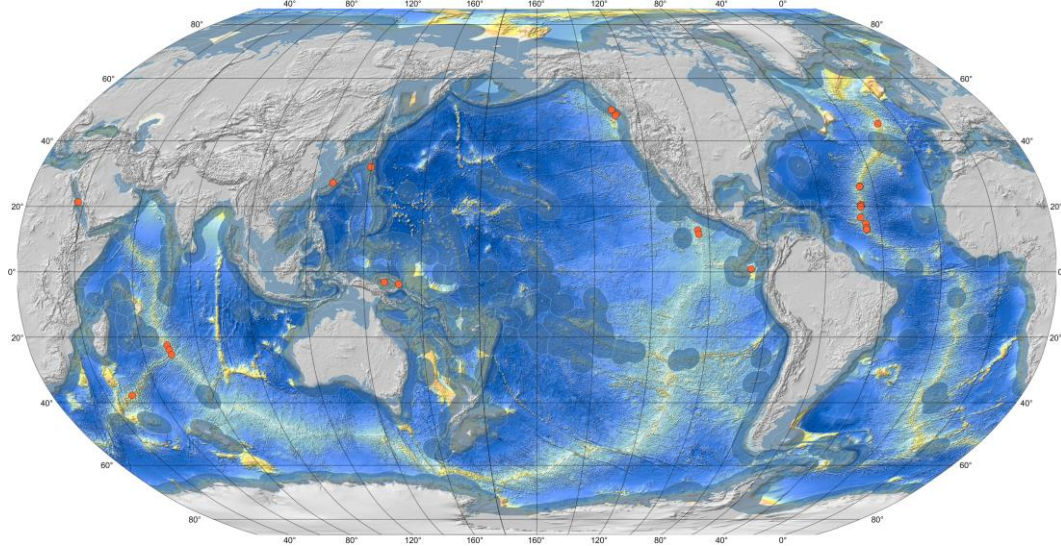
Deposit	Location	Size	drilling tool / vessel	Reference
Atlantis II	Red Sea	90 Mt	coring	Nawab, 1984
TAG	Mid-Atlantic Ridge	4 Mt	ODP-drill ship	Hannington et al., 1998
Middle Valley	Juan de Fuca Ridge	10–15 Mt	ODP-drill ship	Zierenberg et al., 1998
PacManus	Bismarck Sea	small	ODP-drill ship	Binns et al., 2002
PacManus	Bismarck Sea	small	lander-type	Petersen et al., 2005
Solwara 1	Bismarck Sea	2.3 Mt	ROV-based	Lipton et al., 2012
Suiyo	Izu-Bonin Arc	small	lander-type	Marumo et al., 2008
Iheya North	Okinawa Trough	small	IODP-drill ship	Takai et al., 2012
Izena	Okinawa Trough	3.4 Mt	lander-type	Masuda et al., 2014
Fryer , Pika	Mariana Trough	small	lander-type	Takegawa et al., 2008
Logatchev	Mid-Atlantic Ridge	small	lander-type	Petersen et al., 2009

The largest deposits currently known are all at least 100,000 years old, implying that sustained hydrothermal venting over long periods is required to produce significant accumulations of massive sulphide at the seafloor. The growth rate for the main massive sulphide lens (2.7 million tonnes) at the TAG site on the Mid-Atlantic Ridge is about 500 to 1,000 tonnes/yr. Similar growth rates have been estimated for other large deposits on the Mid-Atlantic Ridge (Logatchev, Ashadze, and Krasnov), based on the maximum ages and estimated tonnages of the deposits.

The relatively smaller sizes of most deposits discovered so far are related to the short-lived nature of their heat sources, which include narrow dike injections along the axial zones of the ridges. This is confirmed by age dating indicating that hydrothermal discharge at fast spreading centres is episodic on time scales of only 10 to 100 years. Therefore most sulphide occurrences along the fast-spreading ridges will likely be uneconomic. By contrast, the protracted history of hydrothermal venting at sites like TAG on the slow-spreading Mid-Atlantic Ridge is a consequence of deep-

seated magmatic activity followed by long periods of cooling and release of heat from depth. These deposits are situated in stable structural environments with relatively slow rates of spreading, far from the axis of the ridge. On sedimented ridges, such as Middle Valley on the Juan de Fuca Ridge, long-term heat retention due to a thick impermeable sediment cover may also contribute to the large sizes of such deposits.

Figure A.1.2.5 Location of large seafloor massive sulphide occurrences (estimates above 1 million tonnes; source GEOMAR; N=27). Note that 11 of these occurrences do not contain metals of interest as defined in this study. For another 4 occurrences geochemical data is not yet available.

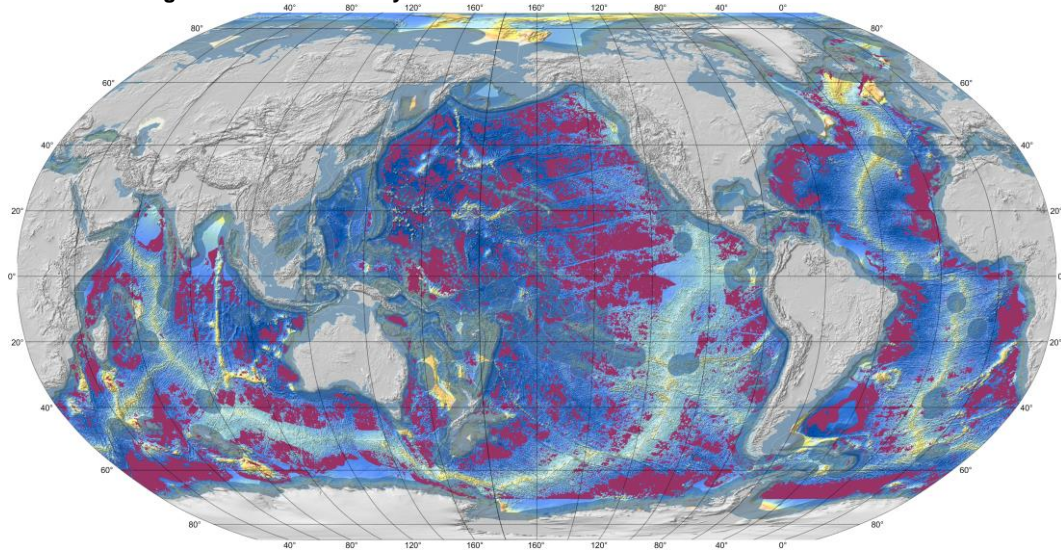


3 Manganese nodules

3.1 The formation and occurrence of manganese nodules

Manganese nodules occur widely on the vast, sediment-covered, plains of the abyssal ocean at depths of about 4,000 to 6,500 m (Fig. A.1.4.1). Manganese nodules are mineral concretions made up of manganese and iron oxides that can be as small as golf balls or as big as large potatoes.

Figure A.1.3.1 Abyssal plains important for manganese nodule formation. The areas were defined by using global basins²¹ and then modified to exclude those with sedimentation rates larger than 2 cm/1000 years and those with an age of less than 10 mio years. Note the lack of data below 70°S.



The manganese and iron minerals in these concretions precipitate from the surrounding seawater in two ways:

- hydrogenetically, in which the minerals precipitate from cold ambient seawater; and
- diagenetically, in which minerals precipitate from sediment pore waters.

The metal oxides that make up the precipitate attach to a nucleus, commonly older nodule fragments, shark teeth or shell fragments, and very slowly build up around the nucleus in layers. Their mineralogy is rather simple and consists of three manganese oxides: vernadite, todorokite, and birnessite as well as a number of non-crystalline Fe-oxihydroxides.

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.

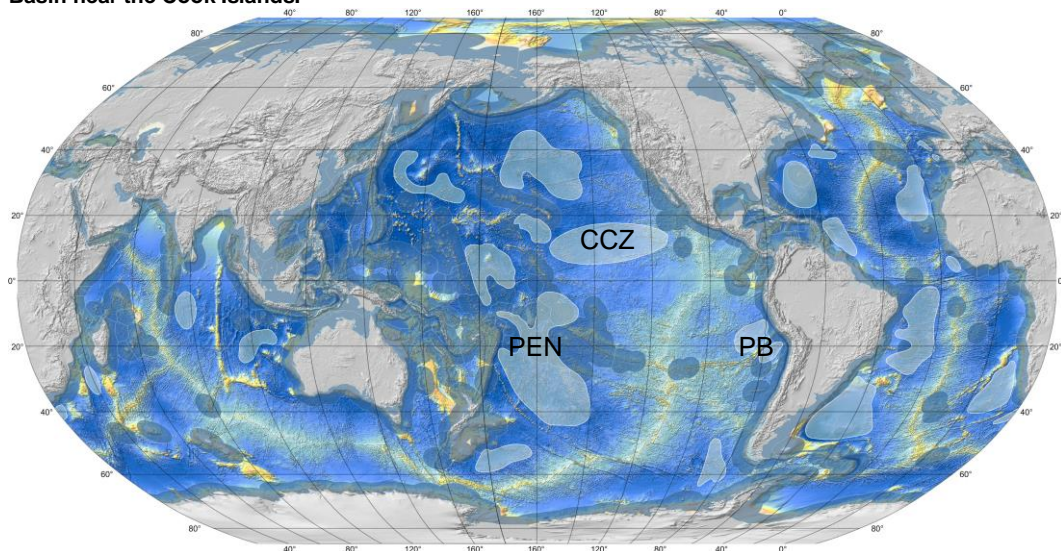
The role of bacteria and organic matter in the formation of nodules is not well understood. The presence of bacteria could indicate a biological role in the formation of the nodules, but the bacteria could also be bystanders caught up in the process of mineralization. The very slow growth rates of nodules suggest that reactions linked with bacteria are not the major mechanisms of manganese

²¹ Based on morphological features identified by GRID Arendal; Harris, P.T., Macmillan-Lawler, M., Rupp, J., Baker, E.K. (2014): Geomorphology of the oceans. *Marine Geology* 352, 4–24.

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 nodules²². 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), which extends from off the west coast of Mexico to as far west as Hawaii (Fig. A.1.4.2). Nodules are also concentrated in the Peru Basin, near the Cook Islands, and at abyssal depths in the Indian and Atlantic oceans. In the CCZ, the manganese 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. The highest percentages of seafloor covered by nodules are found in water depths between 4,100 – 4,200 m, and the highest abundance values are found between 12° to 16° N latitude²³.

Figure A.1.3.2 Area with highest manganese nodule potential based on morphology, age of the crust, and metal input (after Hein et al., 2013). Abbreviations: CCZ = Clarion-Clipperton Zone, PB = Peru Basin, PEN = Penrhyn Basin near the Cook Islands.



Nodule genesis and growth are affected by many environmental factors, especially (1) supply of biogenic, terrigenous and hydrogenetic material to the sediment and to the nodules; (2) deposition and reworking of sediments due to seafloor morphology; (3) bottom water composition and movement; and (4) bioturbation. The high abundance of nodules in the CCZ is attributed to a number of factors. The combination of slow rates of sedimentation and abundant 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.

²² Hein, J.R. and Koschinsky, A. (2013): Deep-ocean ferromanganese crusts and nodules. In: *Treatise on Geochemistry*, 273-291.

²³ ISA (2010): Technical Study No. 6: A Geological Model of Polymetallic Nodule Deposits in the Clarion Clipperton Fracture Zone. International Seabed Authority.

3.2 Metal concentrations and tonnages

Manganese and iron are the principal metals in manganese nodules. The metals of greatest economic interest, however, are nickel, copper, cobalt, and maybe 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 possibly be recovered as by-products (Tab. A.1.4.1). The market for Li is growing rapidly due to its use in batteries, including those in electric and hybrid cars. Lithium in CCZ nodules averages 131 ppm and is especially high in diagenetic nodules of the Peru Basin (mean of 311 ppm²⁴). This is at the lower end of typical Li-bearing salty brines that are exploited on land and contain between 200 and 1 400 ppm Li or pegmatite rocks that contain about 1 % Li²⁵. REE concentrations in nodules are smaller than in ferromanganese crusts, so investigations of possible exploitation of marine resources for REE will likely focus on ferromanganese crusts. Platinum concentrations are much lower in manganese nodules than in ferromanganese crusts, therefore investigations to secure metal supply for this element should also focus on ferromanganese crusts.

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 region²⁶. That would yield nearly 6,000 million tonnes of manganese, more than the entire land-based reserve base of manganese²⁷. Similarly, the amount of nickel (270 million tonnes²⁸) and cobalt (46 million tonnes²⁹) 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 234 million tonnes³⁰ and therefore equals 20 % of the global land-based reserve base³¹. Numerous manganese nodule samples have been taken, however, many of the results, especially from the contractors to the ISA, are not publically available.

We used the sample database of ISA and the distribution of the sample clearly shows a bias to Pacific samples that is related to their higher resource potential (Fig. A.1.4.3). Investigations performed by the ISA itself and working on a larger dataset including proprietary data from the principle contractors shows that the grades are unevenly distributed and that better prospects can be found in the central and northern parts of the CCZ, while the southern, south-western and eastern parts of the CCZ are likely to be unfavourable for nodule deposit occurrence³².

²⁴ Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14

²⁵ Kesler, S.E., Gruber, P.W., Medina, P.A., Keoleian, G.A. Everson, M.P., and Wallington, T.J. (2011). Global lithium resources: relative importance of pegmatite, brine and other deposits *Ore Geology Reviews* 4, 55-69.

²⁶ ISA (2010): Technical Study No. 6: A Geological Model of Polymetallic Nodule Deposits in the Clarion Clipperton Fracture Zone. International Seabed Authority.

²⁷ Hein, J.R. and Koschinsky, A. (2013): Deep-ocean ferromanganese crusts and nodules. In: *Treatise on Geochemistry*, 273-291.

²⁸ ISA (2010): Technical Study No. 6: A Geological Model of Polymetallic Nodule Deposits in the Clarion Clipperton Fracture Zone. International Seabed Authority.

²⁹ ISA (2010): Technical Study No. 6: A Geological Model of Polymetallic Nodule Deposits in the Clarion Clipperton Fracture Zone. International Seabed Authority.

³⁰ *ibid*

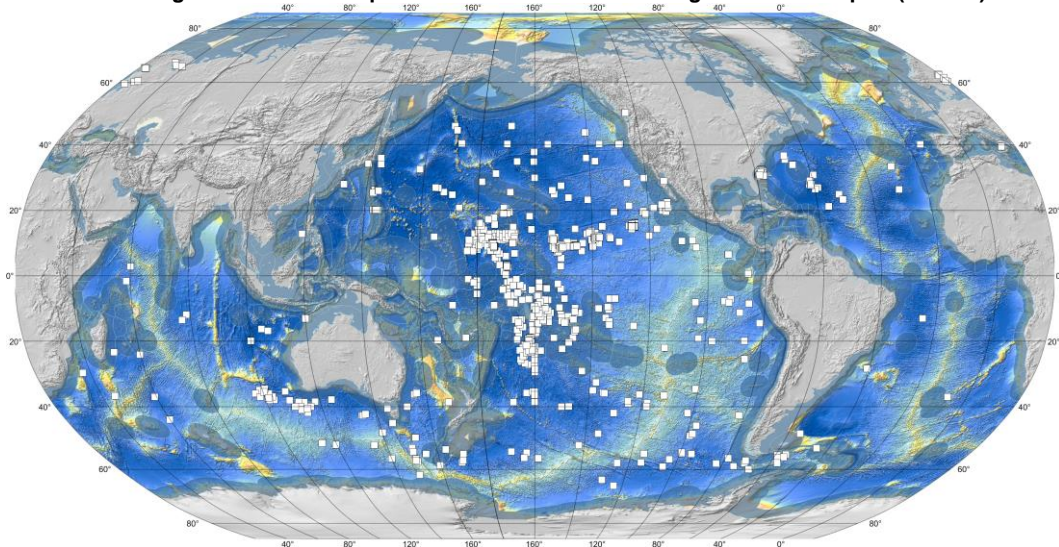
³¹ Hein, J.R. and Koschinsky, A. (2013): Deep-ocean ferromanganese crusts and nodules. In: *Treatise on Geochemistry*, 273-291.

³² ISA (2010): Technical Study No. 6: A Geological Model of Polymetallic Nodule Deposits in the Clarion Clipperton Fracture Zone. International Seabed Authority.

Table A.1.3.1 Mean content of selected elements of manganese nodules in various locations (source Hein et al., 2013).

	Clarion-Clipperton	Indic	Peru Basin	Cook Islands
Mn (%)	28.4	24.4	34.2	17.6
Ni (%)	1.3	1.1	1.3	0.5
Cu (%)	1.1	1.0	0.6	0.2
Co (%)	0.21	0.11	0.05	0.41
Mo (ppm)	590	600	547	-
Li (ppm)	131	110	311	-
REE+Y (ppm)	813	1039	403	-

Figure A.1.3.3 Location of manganese nodule samples in the ISA database investigated for this report (N=2753).



Conservative resource estimates, e.g. neglecting the recovery of trace elements as valuable components, commonly use a combined Cu+Ni+Co grade of > 2.5 wt.% as a cut-off grade for economically feasible future mining operations. Based on this, only few areas of interest remain, mainly in the CCZ (Fig. A.1.4.4). However, the manganese nodules around the Cook Islands are still considered to be a viable resource based on their high Co-content, commonly exceeding 0.5 wt. % Co in individual samples. These concentrations are some of the most Co-rich in the oceans (Fig. A.1.4.5).

Figure A.1.3.4 Location of manganese nodule samples in the ISA database with combined Ni+Cu+Co concentrations above 2.5 wt. % (N=708). Note that most of these samples lie within the Clarion-Clipperton Zone.

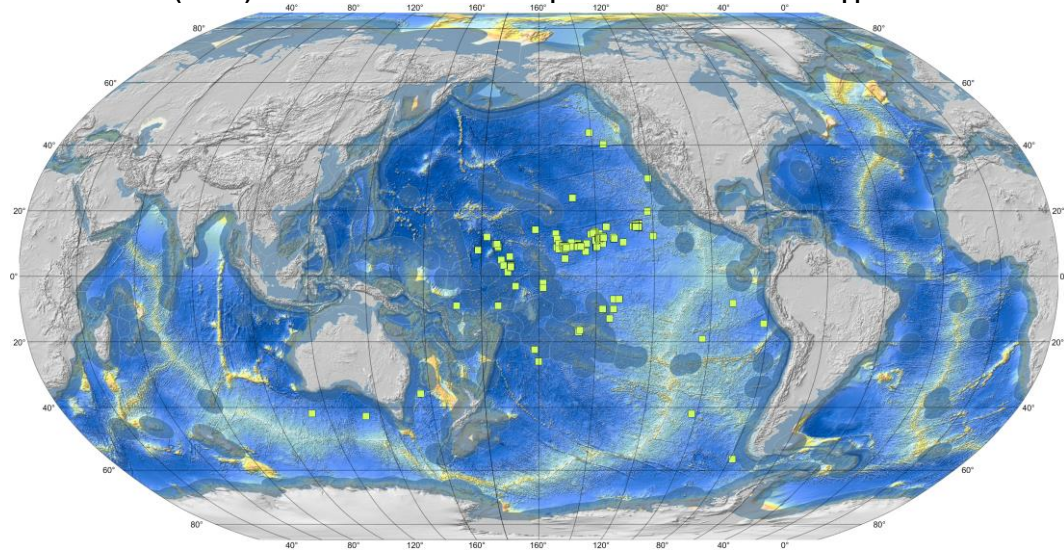
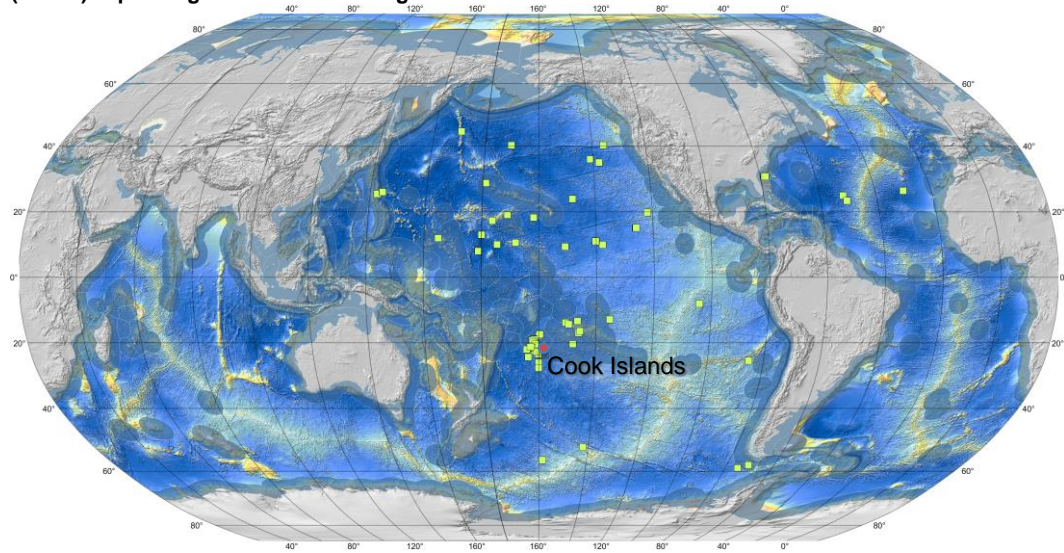


Figure A.1.3.5 Location of manganese nodule samples in the ISA database with Co concentrations above 0.5 wt. % (N=211) explaining the interest in manganese nodules of the Cook Islands.

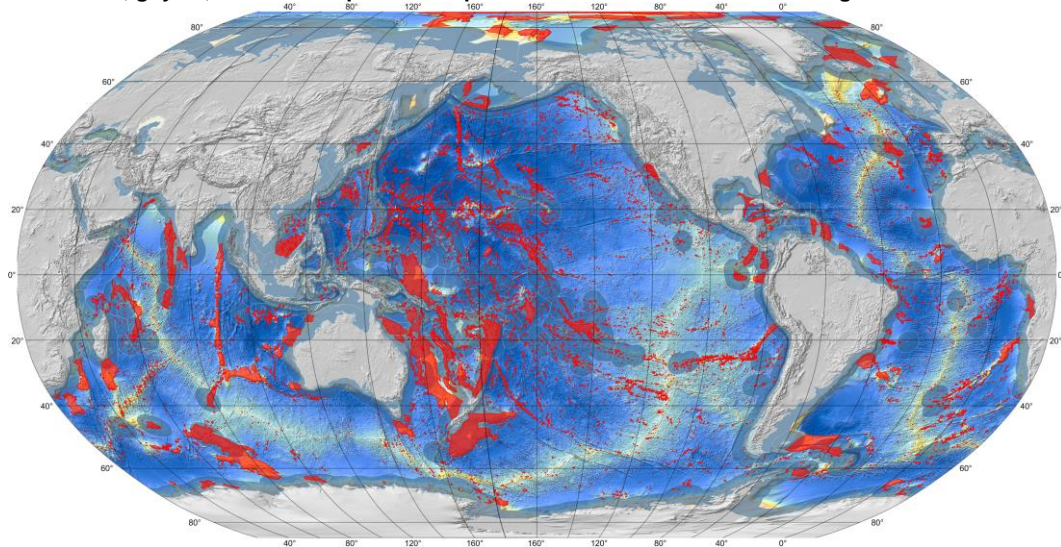


4 Ferromanganese crusts

4.1 The formation and occurrence of manganese nodules

Cobalt-rich ferromanganese crusts precipitate onto nearly all rock surfaces in the deep ocean that are free of sediment. Here, they form pavements of manganese and iron oxides. Ferromanganese crusts may also coat rock pebbles and cobbles. Their thickness varies from less than 1 millimetre to about 260 millimetres. They form at water depths of 600 to 7 000 m on the flanks of volcanic seamounts, ridges, and plateaus. Crusts with sufficient mineral content to be of economic interest commonly occur at depths of about 800 to 2 500 m³³. In the Pacific Ocean, there are more than 11 000 seamounts (57 % of the global total) and 41 000 knolls³⁴ (estimated from the latest global bathymetry), and many more might exist in uncharted waters³⁵. Many seamounts are within the Exclusive Economic Zones (EEZs) of Pacific Island states (Fig. A.1.5.1). The Atlantic Ocean has fewer seamounts, and their cobalt-rich crusts are often associated with hydrothermal activity at sea-floor-spreading centres, with the exceptions of the northeast and northwest continental margin areas.

Figure A.1.4.1 Seamounts, guyots, and oceanic plateaus important for the formation of ferromanganese crust³⁶.



In the Pacific, the manganese and iron oxides precipitate out of cold ambient seawater (hydrogenetic) and are usually 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 sea water are adsorbed onto the manganese and iron oxides. The main source of nearly all metals dissolved in seawater is erosion of the continents. The exception is manganese, which is primarily derived from hydrothermal sources and mixes throughout the global ocean. The metals are adsorbed because of the crusts' very slow growth rates (1 to 5 mm/million years) and the enormous

³³ Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14.

³⁴ Yesson, C., Clark, M.R., Taylor, M.L., Rogers, A.D. (2011): The global distribution of seamounts based on 30 arc seconds bathymetry data. *Deep-Sea Research Part I* 58, 442–453.

³⁵ Kim, S.-S., Wessel, P. (2011) New global seamount census from altimetry-derived gravity data. *Geophysical Journal International* 186, 615–631.

³⁶ Based on morphological features identified by GRID Arendal; Harris, P.T., Macmillan-Lawler, M., Rupp, J., Baker, E.K (2014): Geomorphology of the oceans. *Marine Geology* 352, 4–24.

specific surface area (average 325 m²/cm³ 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, and bismuth; and
- rare-earth elements.

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

Ferromanganese crusts have a simple mineralogy and are composed predominantly of the manganese oxide vernadite and a variety of non-crystalline iron oxyhydroxides. The crusts also contain minor amounts of detrital minerals, such as quartz and feldspar. Ferromanganese crusts vary in thickness from < 1 to 260 mm and are generally thicker on older seamounts. Most thick crusts (greater than about 60 mm) also contain a layer enriched in phosphorous that formed long after the crusts have precipitated from seawater.

Iron and manganese occur in approximately equal amounts in crusts. Cobalt is the trace metal of greatest economic interest and commonly shows values greater than 0.5 wt. % Co. Another metal of great interest is Tellurium (Te), which globally averages about 50 ppm in crusts, with a maximum value of 205 ppm³⁷. The REEs are of great interest because China currently produces about 95% of the total world production. Total REEs average about 0.16% to 0.25% over large regions of the global ocean). However, localized areas can yield total REE concentrations as high as 0.7% and individual samples over 1% total REEs. The trace element platinum may occur with concentrations up to 3 ppm³⁸, however, even on a local scale, Pt does not average more than about 0.7 ppm. Other platinum-group elements (PGEs) are much less concentrated in the crusts. Further metals of interest as potential by-products of Co-Ni-(Mn) mining include Bi, Nb, and Zr (Table A.1.5.1).

The concentration of metals other than iron and manganese in ferromanganese crusts is affected by the concentration of metals in seawater, 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 the manganese oxide vernadite, which is more abundant in crusts than in nodules, and this explains their generally higher concentrations in crusts³⁹. 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 the 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 the rim of terraces and on broad saddles near the summits of seamounts⁴⁰. The central equatorial Pacific region is currently considered the most promising area for crust mining (Fig. A.1.5.2). A rough estimate of the quantity of crusts in the central Pacific region is about 7,533 million dry tonnes⁴¹.

³⁷ Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14.

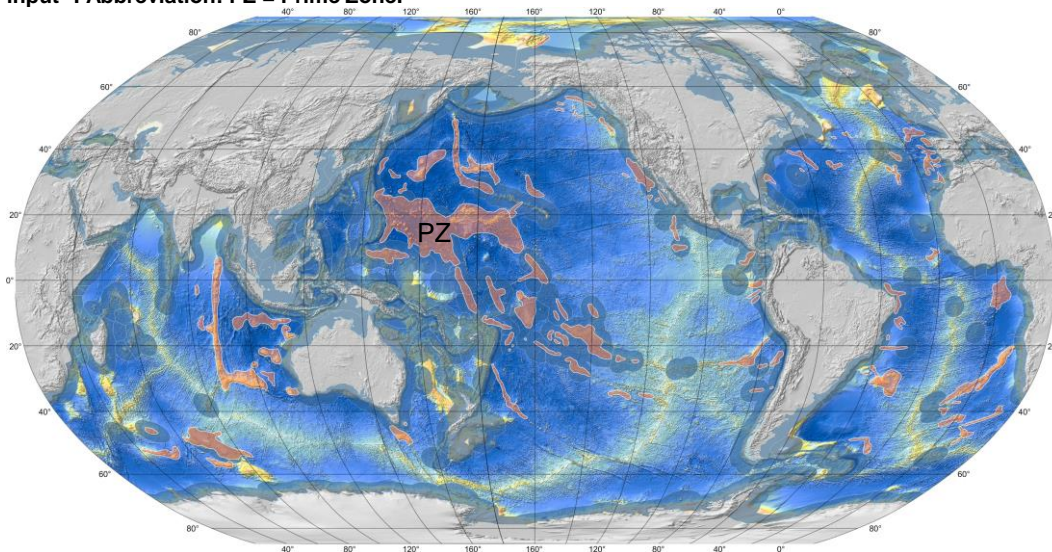
³⁸ Halbach, P., Kriete, C., Prause, B., Puteanus, D. (1989): Mechanisms to explain the platinum concentration in ferromanganese seamount crusts. *Chemical Geology* 76, 95–106; Hein et al., 2000

³⁹ Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14.

⁴⁰ Hein, J.R. (2008): Geologic characteristics and geographic distribution of potential cobalt-rich ferromanganese crusts deposits in the Area. In *Mining cobalt-rich ferromanganese crusts and polymetallic sulphides deposits: Technological and economic considerations*. Proceedings of the International Seabed Authority's Workshop held in Kingston, Jamaica, 31 July-4 August 2006, 59-90.

⁴¹ Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14.

Figure A.1.4.2 Area with highest ferromanganese crust potential based on morphology, age of the crust, and metal input⁴². Abbreviation: PZ = Prime Zone.



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 base⁴³.

Table A.1.4.1 Mean content of selected elements of ferromanganese crusts in various regions (source Hein et al., 2013).

	NW Pacific	S Pacific	Atlantic	Indic
Fe (%)	16.8	18.1	20.9	22.3
Mn (%)	22.8	21.7	14.5	17.0
Ni (%)	0.42	0.46	0.26	0.26
Cu (%)	0.10	0.11	0.09	0.11
Co (%)	0.67	0.62	0.36	0.33
Bi (ppm)	42	22	19	30
Nb (ppm)	54	59	51	61
Pt (ppm)	0.5	0.5	0.6	0.2
REE+Y (ppm)	2454	1634	2402	2541
Te (ppm)	60	30	43	31
Y (ppm)	222	177	181	178
Zr (ppm)	559	754	362	535

Numerous ferromanganese crust samples have been collected, however, many of the results are not publically available. We used the sample database of ISA and the distribution of the samples clearly shows a bias to Pacific samples which is related to their overall higher resource potential (Fig. A.1.5.3; Tab. A.1.5.1). Future resource-related research should focus on the Pacific Ocean based on the higher Co content in ferromanganese crusts from the Pacific when compared to other areas of the global oceans (Fig.A.1.5.4).

⁴² Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14.

⁴³ Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14.

Figure A.1.4.3 Location of ferromanganese crust samples in the ISA database investigated for this report (N=1224).

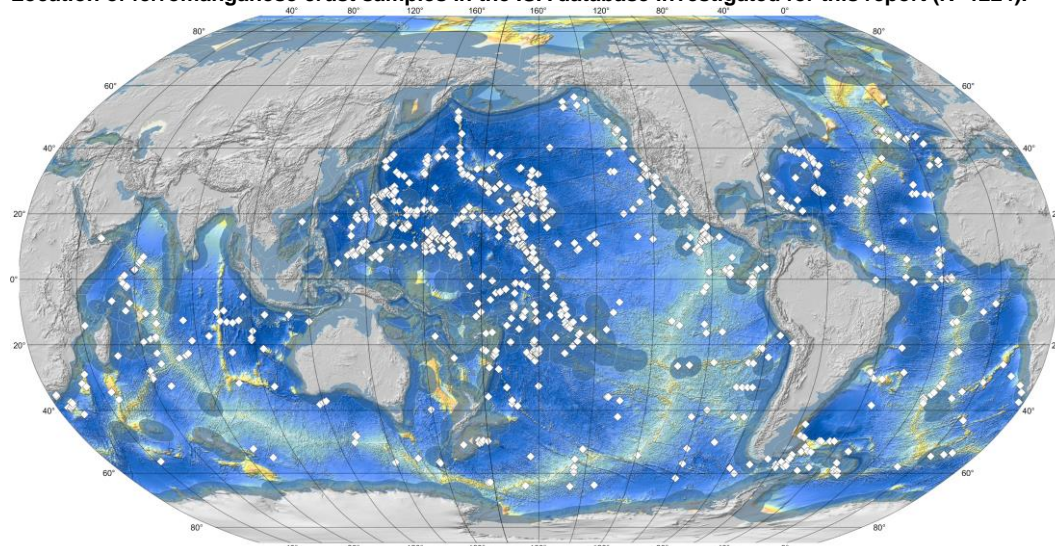
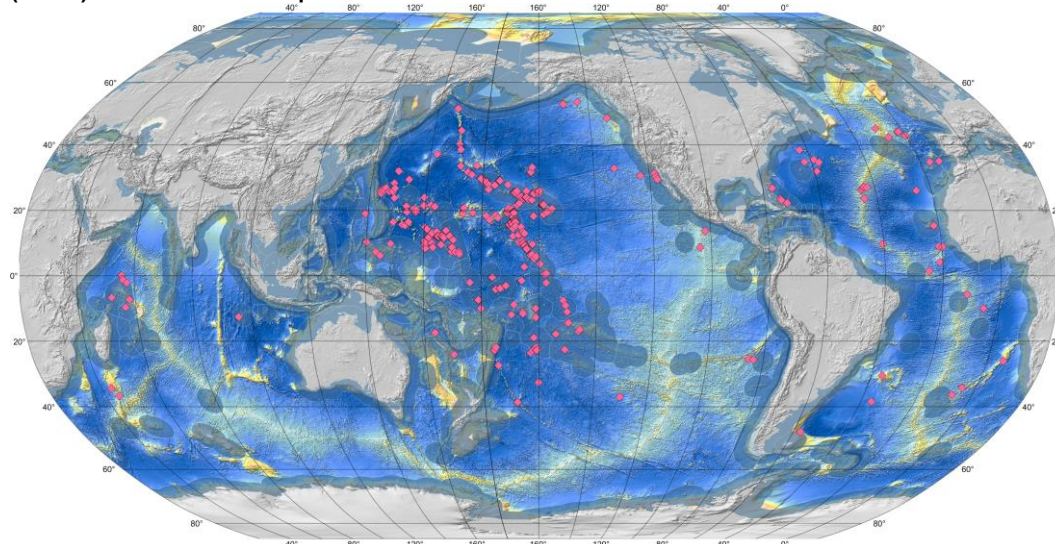


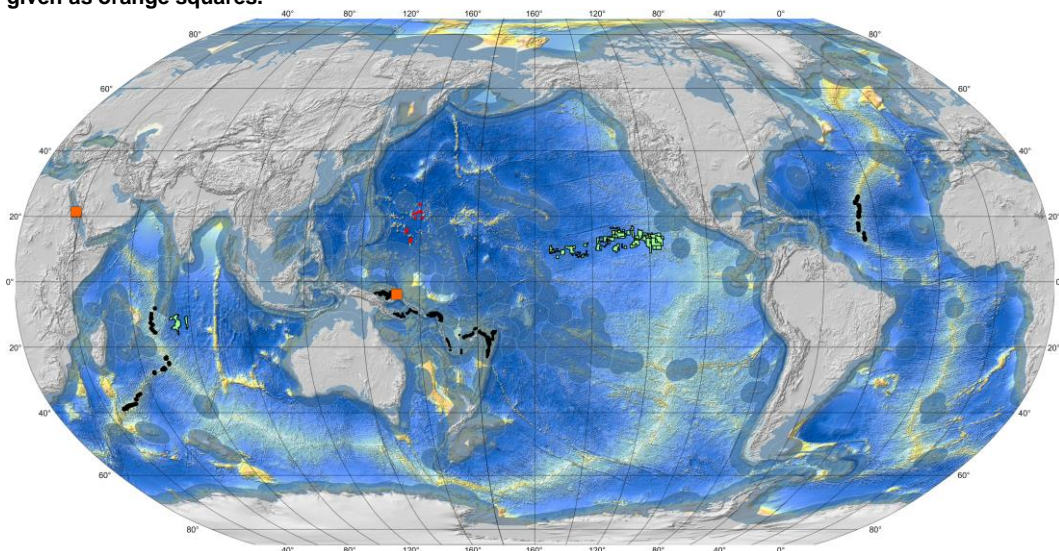
Figure A.1.4.4 Location of ferromanganese crust samples in the ISA database with Co concentrations above 0.5 wt. % (N=465). Note that most samples lie in the western Pacific.



5 Recommendations for areas of future work on marine mineral resources

Current exploration activities involve all three deep-sea marine resources (Fig. A.1.6.1). For **seafloor massive sulphides** 5 licences (10,000 km² each) have been approved by ISA to the following countries: China, Russia, France, Korea and India. One application by Germany for the Indian Ocean will be discussed in July 2014. Additionally Nautilus Minerals holds 203,147 km² of tenements in the western Pacific (in Papua New Guinea, Solomon Islands, Vanuatu, Tonga, and Fiji)⁴⁴ Additional exploration tenements in countries throughout the western Pacific are owned by Neptune Minerals, Bluewater, and other companies, but their exact location is not public. ISA granted 13 licences for **manganese nodules** of which 12 are located in the CCZ and one application (by India) is located in the Indian Ocean. Two further applications for the CCZ are pending (one each by Ocean Mineral Singapore Pte. and UK Seabed Resources). Two licences, from China and Japan, have been approved by ISA for work on ferromanganese crusts in the north-western Pacific. A third application by Russia has not been handled yet. Based on the information given above areas have been defined by the project team as a recommendation for future activities (Figs. A.1.6.1-A.1.6.4). Currently there are only two deep-sea mining licences: since 2010 the Atlantis II Deep in the Red Sea and their metalliferous muds are covered by a 30-year mining licence to a consortium of *Diamond Fields International Ltd* and *Manafa International* covering 60 km² and the Solwara 1 massive sulphides in the Bismarck Sea (Papua New Guinea) held by *Nautilus Minerals Inc*, which was granted in 2011.

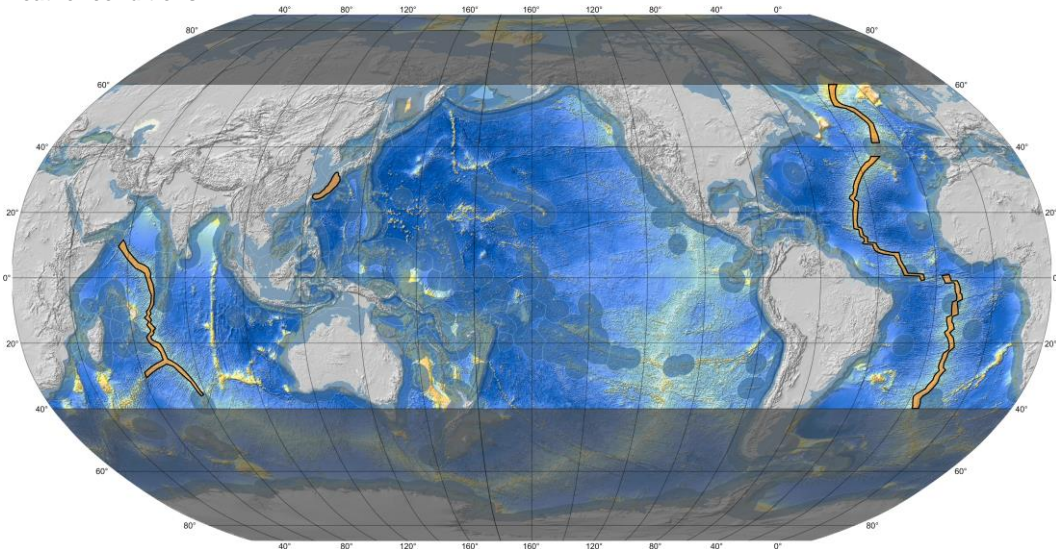
Figure A.1.5.1 Location of exploration licences for seafloor massive sulphides in the Atlantic and Indian Ocean (black), manganese nodules (green) and ferromanganese crusts (red) in the “Area”. Also included are exploration tenements by Nautilus Minerals in the western Pacific (black). Information on tenements from other companies (Neptune, Bluewater, etc.) are not publically available. The location of the only two deep-sea mining licences (Atlantis II Deep in the Red Sea and Solwara 1 in the Bismarck Sea) are given as orange squares.



⁴⁴ Jankowski, P. (2012): NI43-101 Technical Report 2011: PNG, Tonga, Fiji, Solomon Islands, New Zealand, Vanuatu and the ISA (No. NAT008). Nautilus Minerals Inc., 121 pp.

For **seafloor massive sulphides** the main future working areas in the „Area“ are believed to be located along the slow-spreading Mid-Atlantic Ridge and in the Indian Ocean as they seem to host considerable more tonnage than those along the faster spreading segments due to their association with long-lasting faults (Figure A.1.6.2). Presently known sites associated with ultramafic host rocks do only occur in this setting and are more interesting from an economic geology point of view due to their higher Cu and Au content. Areas within the EEZ of Pacific Island states (namely Papua New Guinea, Fiji, Tonga, Solomon Islands and Vanuatu) are also of interest for bilateral work since many of those sites have high Cu and Au contents, however, current knowledge has not indicated sufficient tonnage for mining outside the Manus Basin (e.g. Solwara 1). There is, at present, simply no other massive sulphide occurrence that has been drilled densely enough to provide an economically sound resource estimate. Currently global exploration is performed using tools developed for the discovery of geochemical and geophysical anomalies in the water column. These methods only detect young and hence small deposits. Much more and larger deposits are thought to occur away from the ridge axis and will largely be covered by sediments or a few meters of lava. Clearly, new exploration technologies need to be developed for the detection of such inactive deposits under sediment cover. These sites are more difficult to find due to the lack of surface expressions of the hydrothermal signals. Similarly hydrothermal systems that already form in a sedimented environment (e.g. close to continents) will likely retain most of their metals providing a substantial target for future exploration. Large potential may therefore exist in areas close to continents, for instance in the East China Sea due to the proximity of the continent to the Okinawa Trough back-arc spreading centre.

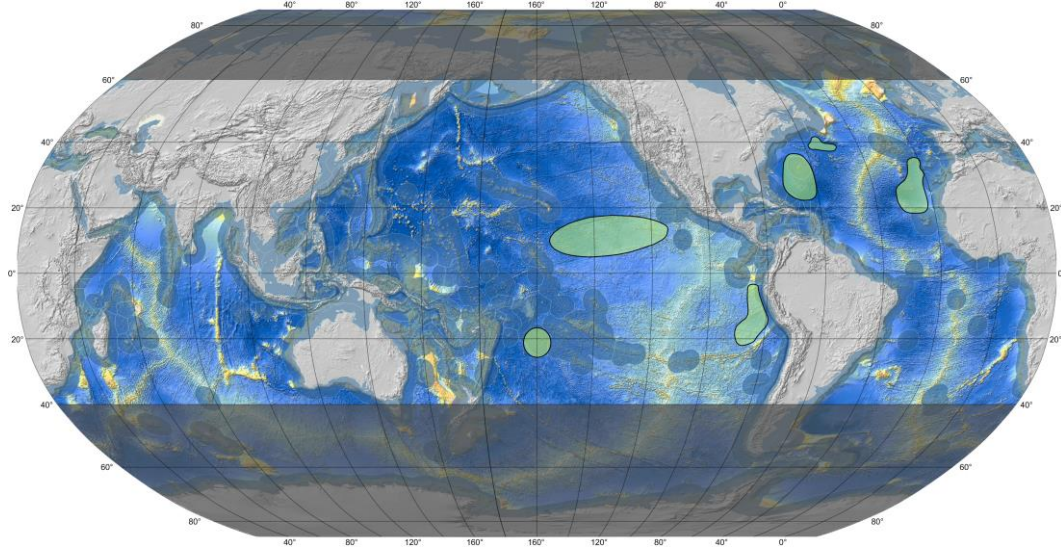
Figure A.1.5.2 Location of possible future area of interest with respect to seafloor massive sulphides. These include the slow-spreading ridges and areas where spreading ridges or back-arcs are close to areas with high sedimentation rates. Grey shaded areas indicate likely limits of ship-based exploitation work due to weather conditions.



For **manganese nodules** (Fig. A.1.6.3) most of the work should be concentrated within the Clarion-Clipperton Zone as this has the largest potential. Additionally, we consider the nodules of the Cook Islands to be a valuable exploration subject due to their Co-content and the areas along the northern Atlantic due to the lack in information. However, the Atlantic sites are, based on current knowledge not a good commercial target. Finally continuing the pioneering work of the DISCOL and

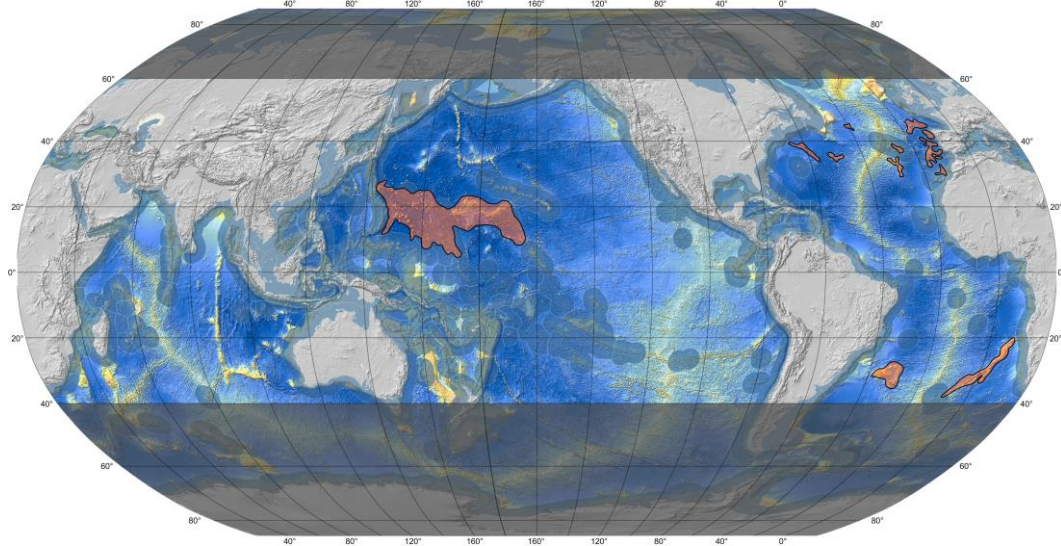
TUSCH projects in the Peru Basin is seen as a valuable contribution in order to further monitor the long-term impact of large-scale disturbances on the deep-sea faunal communities⁴⁵.

Figure A.1.5.3 Location of possible future area of interest with respect to manganese nodules. Grey shaded areas indicate likely limits of ship-based exploitation work due to weather conditions.



Future work with respect to **ferromanganese crusts** should be focussed on the Prime Zone in the western Pacific due to their higher metal grades and thickness (Fig.A.1.6.4). A Few areas near the western and eastern boundaries of the Atlantic are clearly underexplored and might be of interest as well, especially those along the Walfish Ridge and the Rio Grande Rise. However, the metal grades will likely be lower than in the western Pacific.

Figure A.1.5.4 Location of possible future area of interest with respect to ferromanganese crusts. Grey shaded areas indicate likely limits of ship-based exploitation work due to weather conditions.



⁴⁵ Thiel, H., Schriever, G., Ahnert, A., Bluhm, H., Borowski, C., Vopel, K. (2001): The large-scale environmental impact experiment DISCOL—reflection and foresight. Deep Sea Research Part II 48, 3869–3882.

6 References

Literature

- Baker, E.T. (2007): Hydrothermal cooling of midocean ridge axes: Do measured and modeled heat fluxes agree? *Earth and Planetary Science Letters* 263, 140–150.
- Baker, E.T., German, C.R. (2005): On the global distribution of hydrothermal vent fields, in: *Mid-Ocean Ridges: Hydrothermal Interactions Between Lithosphere and Oceans*. American Geophysical Union, Geophysical Monograph 148, pp. 245–265.
- Beaulieu, S.E., Baker, E.T., German, C.R., Maffei, A. (2013): An authoritative global database for active submarine hydrothermal vent fields. *Geochem. Geophys. Geosyst.* 14, 4892–4905.
- Binns, R.A., Barriga, F., Miller, D.J. (2002): Leg 193 summary. *Proceedings of the Ocean Drilling Programme, Initial Reports Vol. 193*, Anatomy of an active felsic-hosted hydrothermal system, Eastern Manus Basin, Texas A&M University.
- Bird, P., (2003): An updated digital model of plate boundaries. *Geochem. Geophys. Geosyst.* 4, 10.1029–2001GC000252.
- Cherkashev, G.A., Ivanov, V.N., Bel'tenev, V., Lazareva, L.I., Rozhdestvenskaya, I.I., Samovarov, M.L., Poroshina, I.M., Sergeev, M.B., Stepanova, T.V., Dobretsova, I.G., Kuznetsov, V.Y. (2013): Massive sulfide ores of the northern equatorial Mid-Atlantic Ridge. *Oceanology* 53, 607–619.
- de Ronde, C.E., Faure, K., Bray, C.J., Chappell, D.A., Wright, I.C. (2003): Hydrothermal fluids associated with seafloor mineralization at two southern Kermadec arc volcanoes, offshore New Zealand. *Mineralium Deposita* 38, 217–233.
- de Ronde, C.E.J., Massoth, G.J., Butterfield, D.A., Christenson, B.W., Ishibashi, J., Ditchburn, R.G., Hannington, M.D., Brathwaite, R.L., Lupton, J.E., Kamenetsky, V.S., Graham, I.J., Zellmer, G.F., Dziak, R.P., Embley, R.W., Dekov, V.M., Munnik, F., Lahr, J., Evans, L.J., Takai, K. (2011). Submarine hydrothermal activity and gold-rich mineralization at Brothers Volcano, Kermadec Arc, New Zealand. *Mineralium Deposita* 46, 541–584.
- Kesler, S.E., Gruber, P.W., Medina, P.A., Keoleian, G.A. Everson, M.P., and Wallington, T.J. (2011). Global lithium resources: relative importance of pegmatite, brine and other deposits *Ore Geology Reviews* 4, 55-69.
- Hannington, M.D., Galley, A.G., Herzig, P.M., Petersen, S. (1998): Comparison of the TAG mound and stockwork complex with Cyprus-type massive sulfide deposits, in: Herzig, P.M., Humphris, S.E., Miller, D.J., Zierenberg, R.A. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results Vol. 158*. Collage Station, TX, pp. 389–415.
- Hannington, M.D., de Ronde, C.D., Petersen, S. (2005). Sea-floor tectonics and submarine hydrothermal systems. *Economic Geology 100th Anniversary Volume* 111–141.
- Hannington, M., Jamieson, J., Monecke, T., Petersen, S., Beaulieu, S. (2011): The abundance of seafloor massive sulfide deposits. *Geology* 39, 1155–1158.
- Harris, P.T., Macmillan-Lawler, M., Rupp, J., Baker, E.K. (2014): Geomorphology of the oceans. *Marine Geology* 352, 4–24.
- Halbach, P., Kriete, C., Prause, B., Puteanus, D. (1989): Mechanisms to explain the platinum concentration in ferromanganese seamount crusts. *Chemical Geology* 76, 95–106.
- Hein, J.R. (2008): Geologic characteristics and geographic distribution of potential cobalt-rich ferromanganese crusts deposits in the Area. In *Mining cobalt-rich ferromanganese crusts and polymetallic sulphides deposits: Technological and economic considerations*. Proceedings of the International Seabed Authority's Workshop held in Kingston, Jamaica, 31 July-4 August 2006, 59-90.
- Hein, J.R. and Koschinsky, A. (2013): Deep-ocean ferromanganese crusts and nodules. In: *Treatise on Geochemistry*, 273-291.
- Hein, J.R., Koschinsky, A., Bau, M., Manheim, F.T., Kang, J.-K., Roberts, L. (2000): Cobalt-rich ferromanganese crusts in the Pacific. In: Cronan, D.S. (Ed.), *Handbook of Marine Mineral Deposits*. CRC Press, Boca Raton, Florida, 239–279.
- Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geology Reviews* 51, 1–14.
- ISA (2010): Technical Study No. 6: A Geological Model of Polymetallic Nodule Deposits in the Clarion Clipperton Fracture Zone. International Seabed Authority.
- Jankowski, P. (2012): NI43-101 Technical Report 2011: PNG, Tonga, Fiji, Solomon Islands, New Zealand, Vanuatu and the ISA (No. NAT008). Nautilus Minerals Inc., 121 pp.

- Kakegawa, T., Utsumi, M., Marumo, K. (2008): Geochemistry of Sulfide Chimneys and Basement Pillow Lavas at the Southern Mariana Trough (12.55°N-12.58°N). *Resource Geology* 58, 249–266.
- Kim, S.-S., Wessel, P. (2011) New global seamount census from altimetry-derived gravity data. *Geophysical Journal International* 186, 615–631.
- Lipton, I. (2012): Mineral Resource Estimate Solwara Project, Bismarck Sea, PNG. Nautilus Minerals Inc., 218 pp.
- Marumo, K., Urabe, T., Goto, A., Takano, Y., Nakaseama, M. (2008): Mineralogy and Isotope Geochemistry of Active Submarine Hydrothermal Field at Suiyo Seamount, Izu-Bonin Arc, West Pacific Ocean. *Resource Geology* 58, 220–248.
- Masuda, N., Okamoto, N., Kawai, T. (2014). Sea-floor massive sulfide mining – its possibility and difficulties to emerge as a future business, in: Drebenstedt, C., Singhal, R. (Eds.), *Mine Planning and Equipment Selection*. Springer International Publishing, 105–112. doi:10.1007/978-3-319-02678-7_11.
- Mottl, M.J. (2003) Partitioning of energy and mass fluxes between mid-ocean ridge axes and flanks at high and low temperature, in: Halbach, P.E., et al., eds., *Energy and mass transfer in marine hydrothermal systems: Dahlem Workshop Report 89*: Berlin, Dahlem University Press, p. 271–286.
- Nawab, Z.A. (1984): Red Sea mining: a new era. *Deep Sea Research Part A. Oceanographic Research Papers* 31, 813–822.
- Petersen, S., Herzog, P.M., Kuhn, T., Franz, L., Hannington, M.D., Monecke, T., Gemmill, J.B. (2005): Shallow Drilling of Seafloor Hydrothermal Systems Using the BGS Rockdrill: Conical Seamount (New Ireland Fore-Arc) and PACMANUS (Eastern Manus Basin), Papua New Guinea. *Marine Georesources & Geotechnology* 23, 175–193.
- Petersen, S., Kuhn, K., Kuhn, T., Augustin, N., Hékinian, R., Franz, L., Borowski, C. (2009): The geological setting of the ultramafic-hosted Logatchev hydrothermal field (14°45'N, Mid-Atlantic Ridge) and its influence on massive sulfide formation. *Lithos* 112, 40–56.
- Takai, K., Mottl, M.J., Nielsen, S.H.H., the IODP Expedition 331 Scientists (2012): IODP Expedition 331: Strong and Expansive Subseafloor Hydrothermal Activities in the Okinawa Trough. *Scientific Drilling* 13, 19–27.
- Thiel, H., Schriever, G., Ahnert, A., Bluhm, H., Borowski, C., Vopel, K. (2001): The large-scale environmental impact experiment DISCOL—reflection and foresight. *Deep Sea Research Part II* 48, 3869–3882.
- Yang, K., Scott, S.D. (1996): Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. *Nature* 383, 420–423.
- Yang, K., Scott, S.D. (2002): Magmatic degassing of volatiles and ore metals into a hydrothermal system on the modern sea floor of the eastern Manus back-arc basin, western Pacific. *Economic Geology* 97, 1079–1100.
- Yesson, C., Clark, M.R., Taylor, M.L., Rogers, A.D. (2011): The global distribution of seamounts based on 30 arc seconds bathymetry data. *Deep-Sea Research Part I* 58, 442–453.
- Zierenberg, R.A., Fouquet, Y., Miller, D.J., Bahr, J.M., Baker, P.A., Bjerkgård, T., Brunner, C.A., Duckworth, R.C., Gable, R., Gieskes, J., Goodfellow, W.D., Gröschel-Becker, H.M., Guerin, G., Ishibashi, J., Iturrino, G.J., James, R.H., Lackschewitz, K.S., Marquez, L.L., Nehlig, P., Peter, J.M., Rigsby, C.A., Schultheiss, P., Shanks, W.C., III, Simoneit, B.R.T., Summit, M., Teagle, D.A.H., Urbat, M., Zuffa, G.G. (1998): The deep structure of a sea-floor hydrothermal deposit. *Nature* 392, 485–488.

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