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Review

Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources

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ABSTRACT

Ferromanganese (Fe–Mn) crusts are strongly enriched relative to the Earth's lithosphere in many rare and critical metals, including Co, Te, Mo, Bi, Pt, W, Zr, Nb, Y, and rare-earth elements (REEs). Fe–Mn nodules are strongly enriched in Ni, Cu, Co, Mo, Zr, Li, Y, and REEs. Compared to Fe–Mn crusts, nodules are more enriched in Ni, Cu, and Li, with subequal amounts of Mo and crusts are more enriched in the other metals. The metal ions and complexes in seawater are sorbed onto the two major host phases, FeO(OH) with a positively charged surface and MnO_2 with a negatively charged surface. Metals are also derived from diagenetically modified sediment pore fluids and incorporated into most nodules. Seafloor massive sulfides (SMS), especially those in arc and back-arc settings, can also be enriched in rare metals and metalloids, such as Cd, Ga, Ge, In, As, Sb, and Se. Metal grades for the elements of economic interest in SMS (Cu, Zn, Au, Ag) are much greater than those in land-based volcanogenic massive sulfides. However, their tonnage throughout the global ocean is poorly known and grade/tonnage comparisons with land-based deposits would be premature.

The Clarion–Clipperton Fe–Mn Nodule Zone (CCZ) in the NE Pacific and the prime Fe–Mn crust zone (PCZ) in the central Pacific are the areas of greatest economic interest for nodules and crusts and grades and tonnages for those areas are moderately well known. We compare the grades and tonnages of nodules and crusts in those two areas with the global terrestrial reserves and resources. Nodules in the CCZ have more Tl (6000 times), Mn, Te, Ni, Co, and Y than the entire global terrestrial reserve base for those metals. The CCZ nodules also contain significant amounts of Cu, Mo, W, Li, Nb, and rare earth oxides (REO) compared to the global land-based reserves. Fe–Mn crusts in the PCZ have significantly more Tl (1700 times), Te (10 times more), Co, and Y than the entire terrestrial reserve base. Other metals of significance in the PCZ crusts relative to the total global land-based reserves are Bi, REO, Nb, and W. CCZ nodules and PCZ crusts are also compared with the two largest existing land-based REE mines, Bayan Obo in China and Mountain Pass in the USA. The land-based deposits are higher grade but lower tonnage deposits. Notably, both land-based deposits have <1% heavy REEs (HREEs), whereas the CCZ has 26% HREEs and the PCZ, 18% HREEs; the HREEs have a much greater economic value. Radioactive Th concentrations are appreciably higher in the land-based deposits than in either type of marine deposit. A discussion of the differences between terrestrial and marine impacts and mine characteristics is also presented, including the potential for rare metals and REEs in marine deposits to be recovered as byproducts of mining the main metals of economic interest in nodules and crusts.

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Contents

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1. Introduction

The occurrence of deep-ocean minerals has been known for more than a century. However, studies dedicated to understanding their genesis, distribution, and resource potential began more recently. Ferromanganese (Fe–Mn) nodules were the first to be studied in detail, with programs fully underway in the 1970s and the mining of nodules in the Clarion–Clipperton Zone (CCZ) anticipated to begin in the late 1970s to early 1980s, which did not take place. Sulfides followed shortly thereafter with discovery of hydrothermal systems along the Galapagos Ridge in 1977 (e.g., Corliss et al., 1979), which was thought to exist because of the discovery of the Red Sea brines and metalliferous muds in 1964–1965 (e.g. Bäcker and Schoell, 1972), and by other indicators (e.g., Scott et al., 1974); the vigorous East Pacific Rise black smoker systems were discovered shortly thereafter, in 1979 (e.g. MacDonald et al., 1980). Study of Fe–Mn crusts as a potential resource for Co gained prominence in the early 1980s (Halbach et al., 1982). Low prices for metals on global markets dampened enthusiasm for mining the deep-ocean until the 2000s, although research and development continued during the intervening time.

Now, three deep-ocean mines are scheduled to start operations within the next two to three years and vast areas of deep-ocean floor have been contracted for exploration, and more contracts are taken out every year (see below). The traditional interests have been in Ni–Cu–Mn for nodules, Co–Ni–Mn for crusts, and Cu–Zn–Au–Ag for seafloor massive sulfides (SMS). Research undertaken in the past ten years has shown that there are additional rare metals and rare-earth elements (REEs) that are potential byproducts of mining of the major metals of interest (e.g., Hein et al., 2010). For example, nodules also have significant concentrations of Co, Li, Mo, REEs, Y, and Zr in addition to the main metals of interest; crusts have high concentrations of Bi, Mo, Nb, Pt, REEs, Te, Th, Ti, W, Y, and Zr; and sulfides in some environments, especially volcanic arcs, may have high concentrations of As, Cd, Ga, Ge, In, Sb, and/or Se.

The metals most enriched in these marine deposits are essential for a wide variety of high-tech, green-tech, emerging-tech, and energy applications (Table 1; Fig. 1). Over the past decade, global consumption of many rare metals has increased, but supplies have not always been reliable due to the limited number of major producers (Table 2). Increased competition for metal resources from rapidly expanding economies (i.e. China, India, Brazil, Indonesia) may cause shortages in the future. Deep-ocean mineral deposits will not replace land-based mining but will offer an additional source of raw materials to meet the increasing demands.

Here, we describe the general characteristics of deep-ocean mineral deposits and their distributions, how the grades and tonnages of deep-ocean deposits compare with land-based resources, the drivers for confronting the challenges of mining the deep seabed, the major players in the development of deep-ocean mineral deposits, and the potential advantages and disadvantages of deep-ocean mining that makes it unique. These comparisons will be mostly confined to Fe–Mn crusts and nodules because the tonnages of SMS in various environments throughout the global ocean are poorly known and grade/tonnage comparisons with land-based deposits have a high degree of uncertainty. However, grades for the main metals of interest (Cu, Zn, Au, Ag) in the SMS deposits are much higher than they are in land-based volcanogenic massive sulfide and porphyry Cu deposits presently being mined.

2. Fe–Mn Crusts

2.1. Distribution and general characteristics

Fe–Mn crusts precipitate from cold ambient bottom waters (hydrogenetic) onto the surface of seamounts, ridges, and plateaus as pavements and coatings on rocks in areas that are kept sediment-free for millions of years (Fig. 2). Crusts are found typically at water depths of 400–7000 m, with the thickest and most metal-rich crusts occurring at depths of about 800–2500 m. The distribution of crusts and characteristics of seamounts indicate that mining operations will likely take place at water depths from about 1500 to 2500 m (Hein et al., 2009). Crusts also occur on ridges in the polar oceans, but their distribution is poorly known. Atlantic and Indian Ocean seamounts and ridges have less Fe–Mn crusts than the Pacific because there are fewer seamounts and sediment-free ridges. Fe–Mn crusts vary in thickness from <1 to 260 mm and are generally thicker on older seamounts (Usui and

Table 1
Rare metals for emerging and next generation technologies.
Modified from Hein (2012) and Tasman Metals LTD website (2012).

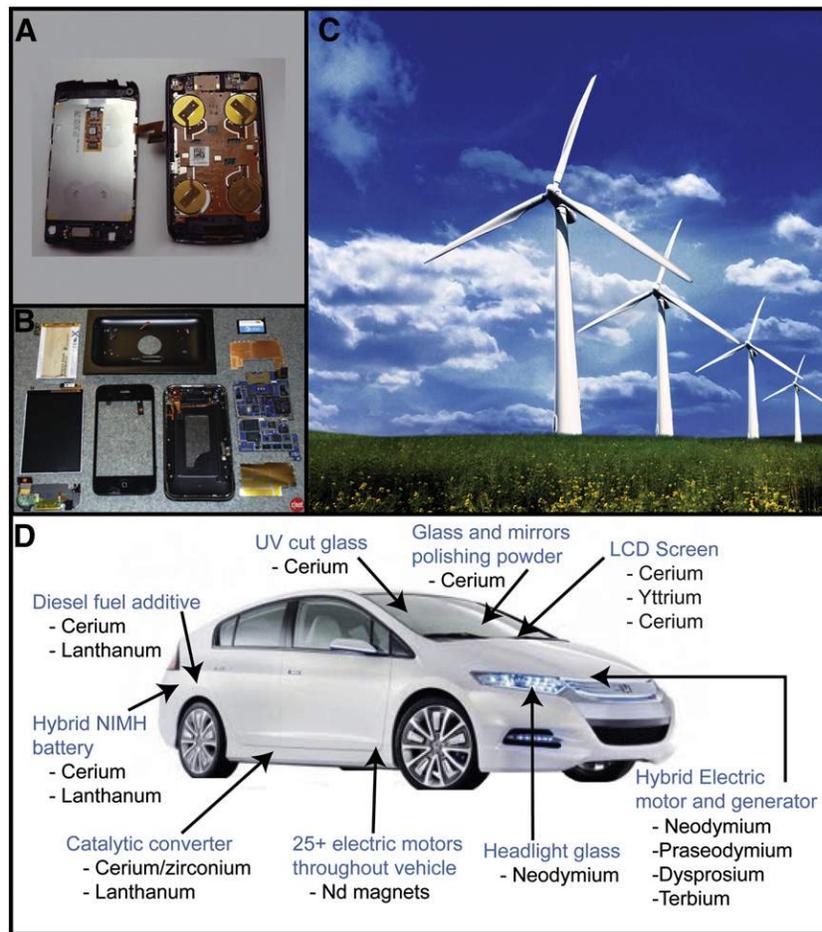| Metal	Application
Tellurium	Photovoltaic solar cells; computer chips; thermal cooling devices
Cobalt	Hybrid & electric car batteries, storage of solar energy, magnetic recording media, high-T super-alloys, supermagnets, cell phones
Bismuth	Liquid Pb–Bi coolant for nuclear reactors; bi-metal polymer bullets, high-T superconductors, computer chips
Tungsten	Negative thermal expansion devices, high-T superalloys, X-ray photo imaging
Niobium	High-T superalloys, next generation capacitors, superconducting resonators
Platinum	Hydrogen fuel cells, chemical sensors, cancer drugs, flat-panel displays, electronics
Yttrium	Compact fluorescent lamps, LEDs, flat-screen TVs, medical applications, ceramics
Neodymium	Hard disk drives, medical applications, portable electronics and small motors, high-strength permanent magnets
Praseodymium	Flat screen TVs, portable electronics and small motors, hard disk drives, magnets, lasers, pigments, cryogenic refrigerant
Cerium	Catalysts, metal alloys, radiation shielding, phosphors for flat screen TVs
Scandium	Super alloys, light aerospace components, X-ray tubes, catalysts
Gadolinium	Magnetic resonance imaging contrast agent, memory chips
Lanthanum	Batteries, optical glass, camera lenses, catalysts for petroleum refining, catalytic converters
Europium	Liquid crystal displays, fluorescent lighting, LEDs, red and blue phosphors for flat screen TVs, portable electronics and small motors
Terbium	Green phosphor for flat screen TVs, lasers, fluorescent lamps, optical computer memories, medical applications

Fig. 1. Rare metal applications in modern high- and green-tech technologies; A and B: Views inside of two popular cell phones, Blackberry® (A) and iPhone® (B), exposing the numerous metal components, many of which contain REEs. A cell phone is on average 25% metal (Urban Mining, 2010). With approximately 1.5 billion cell phones sold in 2010 (MobiThinking, 2011), about 60 kg of tantalum, 510 kg of platinum, 22.5 tonnes of palladium, 51 tonnes of gold, 525 tonnes of silver and 24,000 tonnes of copper were used in cell phone production in one year (Sullivan, 2006; photo A from http://www.pcmag.com/slideshow_viewer/0,3253,l%253D245023%2526a%253D244949%2526po%253D8,00.asp?p=n and photo B from http://news.cnet.com/2300-1041_3-6244920-16.html) C: Giant turbines harness energy from wind; each can contain two-tonne Nd–Fe–B magnets that include 255–320 kg of neodymium. Wind turbines also contain significant amounts of dysprosium, praseodymium, samarium, cobalt, and rhenium (photo from http://serdarguler.deviantart.com/art/Wind-turbines-92959540). D: Diagram of a hybrid car and the many REEs required for its production (adapted from EE Times: Rare earth supply chain: Industry's common cause by Johnson (2010), photo from http://autoshybrid.blogspot.com/2011/04/honda-insights-hybrid-cars.html).

Someya, 1997). Crusts are thickest in the NW Pacific where the sea-mounts are as old as Jurassic age, the oldest in the global ocean. NW equatorial Pacific crusts also typically have the highest concentrations of rare metals. For these reasons, the NW-central equatorial Pacific is considered the prime zone for crust exploration (PCZ; Fig. 3).

Fe–Mn crusts have very high porosity (mean 60%), extremely high specific-surface areas (mean 325 m^2/g), and grow at incredibly slow rates of 1–5 mm/Ma, all of which allow for the sorption of considerable quantities of metals from seawater (Hein et al., 2000). In fact, sorption of metals onto crusts and nodules is significant enough to control the concentrations (e.g. Ce, Te) and redox state (e.g. Te) of some elements in seawater (Hein et al., 2003).

Seamounts and ridges have characteristics that aid in the development of Fe–Mn crusts and the acquisition of metals. For example, obstructional upwelling along the flanks of seamounts creates turbulent mixing along the flanks and over the summits that help keep seamounts sediment free and this upwelling supplies nutrients to surface waters to be utilized in primary productivity. Organic matter from primary productivity sinks and oxidizes in the water column creating an oxygen-minimum zone, which acts as a reservoir for dissolved Mn and its associated metals, and also slows down the growth rates of crusts thereby allowing for maximum time possible for the acquisition of metals from ocean water.

2.2. Mechanism of formation

Hydrogenetic accretion of Fe–Mn crusts is controlled by the precipitation of colloids of hydrated Mn and Fe oxides, which acquire trace metals by surface sorption processes. An electrochemical model describes a first-order process for acquisition of metals from seawater, with positively charged ions sorbed onto the negatively charged surface of MnO_2 and negatively charged and neutral ions in seawater sorbed onto the slightly positive charged surface of $FeO(OH)$ (Fig. 4). During this formation of surface metal complexes, both electrostatic and chemical bonding may play a role in the accumulation of trace metals. Second-order processes include surface oxidation (e.g., Co, Pt, Te, Ce, Tl), substitution, and possibly precipitation of discrete phases (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003). The sorption and subsequent surface oxidation reactions secure the metals from desorption through formation of covalent bonds (Hein and Koschinsky, 2013).

2.3. Mineralogical and chemical compositions

Fe–Mn crusts are composed of two X-ray reflection δ-MnO_2 (vernadite) and X-ray amorphous Fe oxyhydroxide ($FeO(OH)$). Todorokite is rare, found in only 2% of open-ocean Pacific crusts (Hein et al., 2000). Carbonate fluorapatite (CFA) can make up more than 20%

Table 2
Leading global metal producers, with China highlighted[a].
Data from Price (2010), Society of Economic Geologists Newsletter, No. 82, July 2010.

Element	Leading Producer	2nd Producer	3rd Producer
Aluminum	Australia (31%)	China (18%)	Brazil (14%)
Arsenic	China (47%)	Chile (21%)	Morocco (13%)
Cadmium	China (23%)	Korea (12%)	Kazakhstan (11%)
Chromium	South Africa (42%)	India (17%)	Kazakhstan (16%)
Cobalt	Congo (40%)	Australia (10%)	China (10%)
Copper	Chile (34%)	Peru (8%)	USA (8%)
Gallium	China	Germany	Kazakhstan
Germanium	China (71%)	Russia (4%)	USA (3%)
Gold	China (13%)	Australia (9%)	USA (9%)
Helium	USA (63%)	Algeria (19%)	Qatar (12%)
Indium	China (50%)	Korea (14%)	Japan (10%)
Iron	China (39%)	Brazil (17%)	Australia (16%)
Lead	China (43%)	Australia (13%)	USA (10%)
Lithium	Chile (41%)	Australia (24%)	China (13%)
Manganese	China (25%)	Australia (17%)	South Africa (14%)
Molybdenum	China (39%)	USA (25%)	Chile (16%)
Nickel	Russia (19%)	Indonesia (13%)	Canada (13%)
Niobium	Brazil (92%)	Canada (7%)	——
Palladium	Russia (41%)	South Africa (41%)	USA (6%)
Platinum	South Africa (79%)	Russia (11%)	Zimbabwe (3%)
Rare Earths	China (97%)	India (2%)	Brazil (1%)
Selenium	Japan (50%)	Belgium (13%)	Canada (10%)
Silver	Peru (18%)	China (14%)	Mexico (12%)
Tellurium	Chile	USA	Peru
Tin	China (37%)	Indonesia (33%)	Peru (12%)
Uranium	Canada (21%)	Kazakhstan (19%)	Australia (19%)
Vanadium	China (37%)	South Africa (35%)	Russia (26%)
Zinc	China (25%)	Peru (13%)	Australia (12%)

[a] Elements highlighted in blue are common in marine mineral deposits.

of older layers (pre-middle Miocene) of thick crusts. CFA is formed by diagenetic processes during times of major global climate transitions (Hein et al., 1993; Koschinsky et al., 1997). Goethite occurs in the
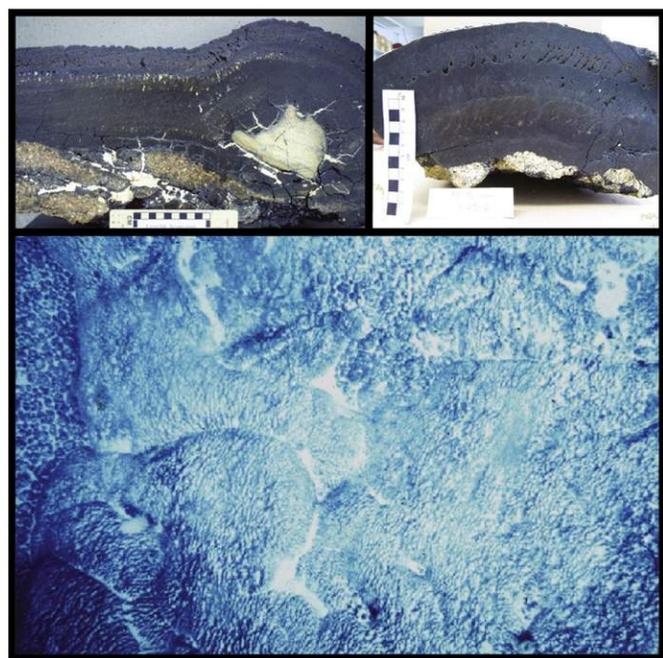

Fig. 2. Photo of seabed at 2000 m water depth showing Fe–Mn crust pavement (~4 m by 3 m) on Horizon Guyot, Central Pacific, with two photos of Fe–Mn crusts: Upper left is an 18 cm-thick crust (D11-1) from 1780 m water depth in the Marshall Islands EEZ that started growing about 72 Ma ago onto a substrate rock; upper right is a 12 cm-thick crust (CD29-2; cruise F7-86-HW) from the Johnston Island EEZ (USGS photos, Hein).

older layers of about 6% of crusts in the Pacific, formed either through the maturation of the X-ray amorphous FeO(OH) (Hein et al., 2000) or formation of the crust in a suboxic paleoenvironment, possibly during precipitation of the CFA (Koschinsky et al., 1997). Minor quartz, feldspar, and other detrital minerals in the crusts are delivered by winds and by weathering of local outcrops.

Fe and Mn occur in subequal amounts in crusts with Mn generally higher in open-ocean environments in the Pacific and Fe generally somewhat higher in Atlantic and Indian Ocean crusts and in continental-margin crusts around the Pacific (Table 3). Traditionally, Co and secondarily Ni have been the metals of greatest economic interest in Fe–Mn crusts, and mean concentrations for large areas of the global ocean range from 0.30% to 0.67% and 0.23% to 0.46%, respectively (Table 3). Smaller areas that would compose a 20-year mine site (Hein et al., 2009) could average about 0.8% Co and 0.5% Ni. Another metal of great interest to the photovoltaic solar cell industry is Te, which globally averages about 50 ppm in crusts, with a maximum value of 205 ppm (Hein et al., 2003, 2010). The REEs are of great interest because China currently produces about 95% of the total world production and is yearly decreasing the amounts exported because of increased internal demand. Total REEs average about 0.16% to 0.25% over large regions of the global ocean (Table 3). However, localized areas can yield total REE concentrations as high as 0.7% and individual samples over 1% total REEs. Platinum has also received attention because values as high as 3 ppm have been reported (Halbach et al., 1989; Hein et al., 2000). However, for most locations, even for the small, localized area of a mine site, Pt does not average more than about 0.7 ppm, which is still significant compared to land-based deposits if extractive metallurgy can be optimized. All the other platinum-group elements (PGEs) Rh, Ru, Os, Pd, and Ir are enriched over the Earth's crustal average, but are much less concentrated in Fe–Mn crusts than Pt. Mean concentrations of other metals of interest as potential byproducts of Co-Ni-Mn mining (Bi, Mo, Nb, Th, Ti, W, Zr) are listed in Table 3.

3. Fe–Mn nodules

3.1. Distribution and general characteristics

Fe–Mn nodules occur throughout the global ocean, predominantly on the surface of sediment-covered abyssal plains at water depths of approximately 3500 to 6500 m (Fig. 5). Some nodules are partly buried in the sediment and others are completely buried. The most extensive deposits have been found in the Pacific Ocean, especially between the Clarion and Clipperton Fracture Zones (CCZ), the Peru Basin, and Penrhyn-Samoa Basins. A large nodule field also occurs in the Central Indian Ocean basin (Fig. 6); fields may also occur in the Argentine Basin in the SW Atlantic and in the Arctic Ocean, although those areas are poorly explored. The CCZ is the area of greatest economic interest and is an area where 13 exploration contracts of about 75,000 km² each (one exception of 58,620 km²) have been signed or are pending to be signed with the International Seabed Authority (see below). This interest is because of high Ni and Cu concentrations found in the CCZ nodules and high nodule abundances.

Nodules are abundant in abyssal areas with oxygenated bottom waters, low sedimentation rates (less than 10 cm/ka), and where sources of abundant nuclei occur. High-grade nodules occur in areas of moderate primary productivity in surface waters (ISA, 2010). The location of nodule growth relative to the calcite compensation depth (CCD), which is controlled by primary productivity in surface waters, is important because above that depth biogenic calcite increases sedimentation rates and dilutes organic matter contents necessary for diagenetic reactions in the sediments that release Ni and Cu (Cronan, 2006; Verlaan et al., 2004). The highest-grade nodules form near, but generally below, the CCD.

Nodules generally range from about 1 to 12 cm in their longest dimension, with the low- to middle-range typically the most common
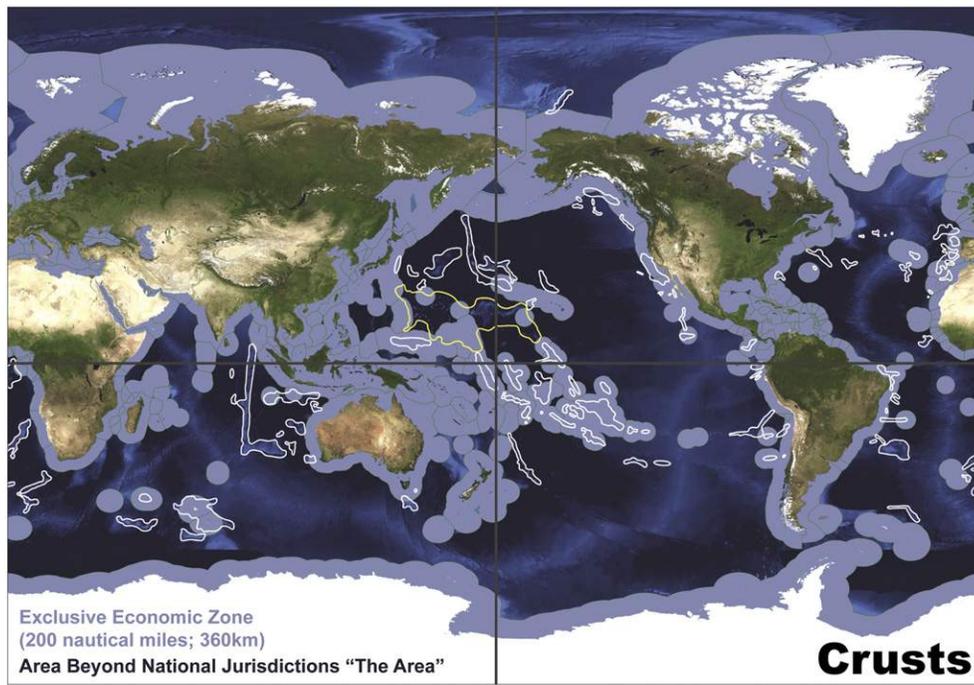
Fig. 3. Map of global distribution of Exclusive Economic Zones (gray shading), areas beyond national jurisdictions (dark black-blue to pale gray-blue), and global permissive areas for cobalt-rich crust development; the central Pacific prime crust zone (PCZ) is the zone of greatest economic interest and is marked by a yellow line; all other areas are marked with a white line; a permissive area does not mean that economic crust deposits will be found in that area. The equator and 180th parallel are marked by gray lines.

(1–5 cm). Based on measurements of 6706 nodules from the CCZ, Morgan (2000) determined the median maximum, middle, and minimum nodule dimensions to be 8, 6, and 4 cm, respectively; however, nodules smaller than 2 cm were not considered in his analysis. Diagenetic nodules up to 20 cm in their maximum dimension have been found in the Peru Basin (von Stackelberg, 2000). The mean dry bulk density (1.35 g/cm^3) and mean porosity (60%) for nodules (Jauhari and Pattan, 2000) are comparable to those for crusts. The highly variable mean specific surface area of Fe–Mn nodules (~150 m^2/g) is significantly less than the 325 m^2/g characteristic of crusts.
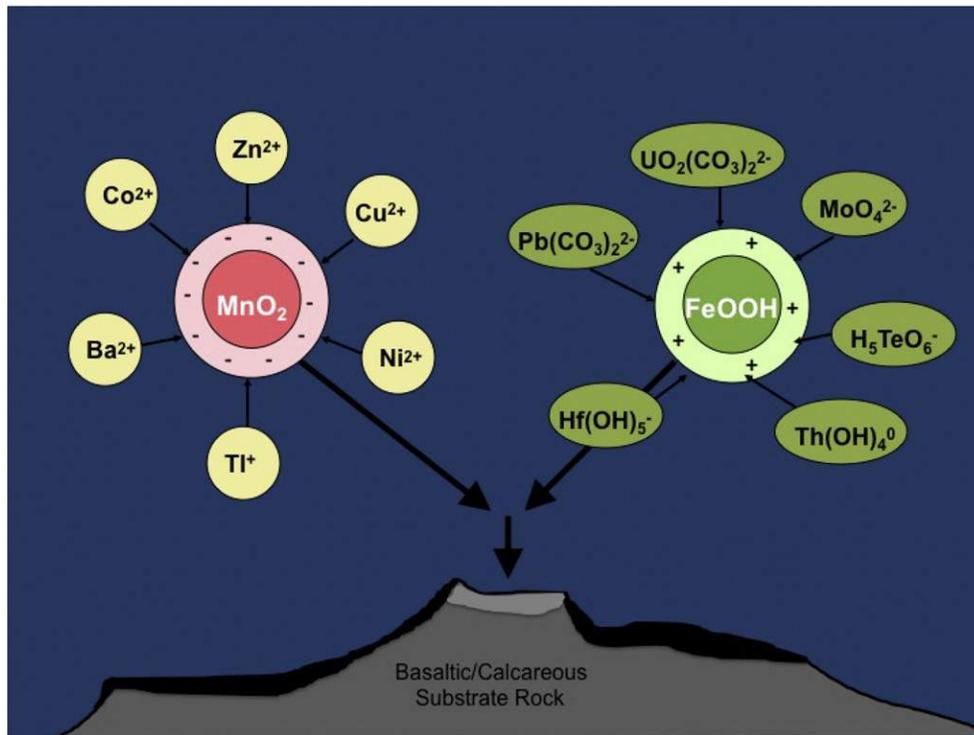

Fig. 4. Simplified electrochemical model of sorption of dissolved metal species on Fe and Mn phases in seawater, which are precipitated as a pavement on the flanks and summit of seamounts. Formation of colloidal or particulate Mn and Fe oxides is followed by sorption of oppositely charge ions on the charged surfaces of the oxide phases. Modified from Koschinsky and Halbach (1995).

Table 3

Compiled chemical composition of crusts and nodules from selected areas of the global ocean (see Fig. 2)[a].

Crust and nodule data modified from Hein et al. (2000) and Hein and Koschinsky (2013).

Element	Atlantic Ocean Mean	N	Indian Ocean Mean	N	N. Pacific Prime Zone Mean	N	Non-Prime N. Pacific Mean	N	S. Pacific Mean	N	CA margin Mean	N	CCZ nodules Mean	N	Peru Basin nodules Mean	N	Indian Ocean nodules[b] Mean	N
Fe (wt%)	20.9	43	22.3	23	16.8	368	22.5	70	18.1	286	23.5	167	6.16	66	6.12		7.14	1135
Mn	14.5	43	17.0	23	22.8	368	23.4	70	21.7	321	18.2	167	28.4	66	34.2		24.4	1135
Si	5.21	43	6.82	23	4.04	309	5.88	70	4.75	255	11.2	167	6.55	12	4.82		10.02	36
Al	2.20	43	1.83	23	1.01	357	1.80	69	1.28	241	1.84	167	2.36	65	1.50		2.92	49
Mg	1.58	43	1.25	23	1.10	334	1.37	70	1.32	192	1.23	167	1.89	66	1.71		1.99	53
Ca	4.03	43	2.27	23	4.03	334	2.54	70	3.53	256	2.14	167	1.70	66	1.82		1.67	53
Na	1.26	43	1.55	23	1.63	309	1.98	70	1.52	88	1.99	167	1.99	66	2.65		1.86	38
K	0.54	43	0.63	23	0.54	309	0.78	70	0.63	156	0.85	167	0.99	66	0.81		1.14	49
Ti	0.92	43	0.88	23	1.16	351	1.01	70	1.12	230	0.66	167	0.32	66	0.16		0.42	53
P	0.75	43	0.38	23	0.97	334	0.95	70	0.78	265	0.55	167	0.21	66	0.15		0.17	46
Cl	>0.74	31	>1.00	19	0.91	49	>1.08	40	>1.05	40	0.88	3	0.27	12	>0.50		–	–
LOI	26.0	43	26.6	23	32.0	191	25.3	70	18.5	55	14.7	105	26.5	12	16.2		–	–
H₂O⁻	10.6	43	14.1	23	19.4	309	17.4	70	19.8	53	17.7	167	11.6	12	–		–	–
H₂O⁺	–	–	–	–	7.99	263	9.20	27	10.2	7	9.39	63	8.80	7	–		–	–
CO₂	–	–	–	–	0.74	263	0.69	27	0.83	7	0.37	63	–	–	–		–	–
S_T	0.25	31	0.15	9	0.27	49	0.18	40	0.17	40	0.09	3	0.17	12	–		–	–
Ag (ppm)	0.20	18	0.37	9	0.1	4	1.5	9	0.97	13	1.2	83	0.17	12	0.05		–	–
As	308	42	207	19	389	334	257	66	287	84	252	167	67	12	65		150	3
Au (ppb)	6.0	2	21	2	55	13	25	21	33	38	6.6	10	4.5	9	–		–	–
B (ppm)	257	13	287	10	178	43	302	40	197	40	351	3	–	–	–		–	–
Ba	1556	43	1533	23	1938	334	2267	70	1705	143	2224	167	3500	66	3158		1708	42
Be	9.0	43	6.9	23	5.9	49	7.4	43	5.4	59	4.1	105	1.9	12	1.4		–	–
Bi	19	38	30	22	42	40	31	41	22	46	16	105	8.8	12	3.3		–	–
Br	36	10	54	6	28	34	29	36	30	72	27	3	–	–	–		–	–
Cd	4.1	34	3.5	18	3.6	291	3.7	66	4.1	62	3.5	167	16	12	19		18	3
Co	3608	43	3291	23	6655	368	3733	70	6167	321	2977	167	2098	66	475		1111	1124
Cr	47	40	22	18	28	278	30	63	35	79	52	167	17	12	16		18	3
Cs	–	–	5.0	1	3.7	1	5.8	20	1.9	18	0.58	102	1.5	61	0.78		0.99	3
Cu	861	43	1105	23	982	368	1074	70	1082	321	438	167	10,714	66	5988		10,406	1124
Ga	15	39	16	23	18	39	18	35	29	27	11	37	36	12	32		–	–
Ge	0.66	18	0.64	9	–	–	15	8	2.4	11	0.96	69	–	–	0.60		–	–
Hf	8.7	30	9.8	15	9.2	49	6.9	30	9.1	81	6.3	105	4.7	66	4.7		14	3
Hg (ppb)	86	37	38	18	9.3	12	28	37	32	33	14	65	18	3	16		–	–
In (ppm)	0.18	19	0.26	10	0.60	7	0.79	12	0.87	6	0.14	74	0.27	12	0.08		–	–
Li	33	42	8.3	22	3.3	38	7.3	41	3.5	36	15	3	131	66	311		110	38
Mo	409	43	392	23	463	334	516	70	418	67	354	167	590	66	547		600	38
Nb	51	43	61	23	54	49	50	42	59	46	31	105	22	66	13		98	3
Ni	2581	43	2563	23	4216	368	3495	70	4643	321	2299	167	13,002	66	13,008		11,010	1124
Pb	1238	43	1371	23	1636	332	1470	70	1057	113	1541	167	338	66	121		731	38
Rb	15	24	16	17	14	18	15	33	11	27	13	105	23	66	12		70	3
Sb	51	30	40	15	41	49	52	34	35	73	34	105	41	12	61		50	3
Sc	16	43	13	23	7.0	49	11	43	9.3	82	9.6	105	11	66	7.6		25	3
Se	0.44	10	1.7	10	2.8	6	13	23	5.1	14	1.0	98	0.72	12	0.50		–	–
Sn	8.3	28	9.7	17	13	16	9.0	18	11	34	3.3	98	5.3	12	0.90		–	–
Sr	1262	43	1201	23	1513	309	1608	70	1483	67	1276	150	645	66	687		709	53
Ta	1.3	17	0.91	10	1.2	8	3.1	28	1.2	47	0.75	101	0.33	66	0.23		1.8	3
Te	43	37	31	22	60	49	30	33	38	38	11	101	3.6	66	1.7		40	3
Tl	104	38	95	22	160	40	123	41	154	46	41	105	199	12	129		347	3
Th	52	42	56	18	12	46	36	39	15	67	53	105	15	66	6.9		76	3
U	11	35	10	18	12	44	13	37	12	67	12	105	4.2	66	4.4		16	3
V	849	43	634	23	642	334	679	70	660	177	613	167	445	66	431		497	16
W	79	35	80	18	89	42	87	37	97	56	59	105	62	66	75		92	3
Y	181	43	178	23	222	300	190	62	177	49	169	167	96	66	69		108	38
Zn	614	43	531	23	669	331	673	70	698	181	561	167	1366	66	1845		1207	692
Zr	362	38	535	22	559	49	724	41	754	46	473	105	307	66	325		752	3
La	272	42	290	21	338	89	320	45	204	75	269	115	114	66	68		129	50
Ce	1392	42	1469	21	1311	89	1360	45	818	75	1351	115	284	66	110		486	24
Pr	63.8	20	66.2	12	61.0	89	61.2	40	40.8	31	60.4	115	33.4	66	14.1		33.0	37
Nd	243	42	259	21	255	89	275	45	184	67	253	115	140	66	63		146	50
Sm	55.5	20	60.8	12	51.3	89	56.8	40	38.1	67	53.5	115	34.0	66	14.0		32.4	50
Eu	11.5	42	12.5	21	12.4	89	13.7	45	17.5	75	13.4	115	8.03	66	3.87		7.83	46
Gd	57.9	20	67.2	12	55.8	89	66.3	40	43.9	31	55.4	115	31.8	66	15.6		32.0	24
Tb	9.17	20	9.99	12	8.73	88	9.55	40	5.98	53	8.83	115	4.98	66	2.52		5.00	37
Dy	47.1	20	55.6	12	59.2	89	56.0	40	40.7	30	48.7	115	28.5	66	15.8		26.5	46
Ho	9.61	41	10.6	13	10.9	88	10.8	43	8.45	17	9.70	115	5.35	66	3.42		4.92	46
Er	28.0	20	29.3	12	30.9	89	31.3	40	26.5	31	27.4	115	14.6	66	9.80		12.9	24
Tm	3.91	20	4.03	12	4.54	88	4.26	40	3.60	17	3.83	115	2.11	66	1.49		2.00	11
Yb	23.9	42	24.8	21	28.5	89	28.3	45	21.9	75	24.9	115	13.7	66	10.3		11.8	46
Lu	3.74	20	4.05	12	4.30	46	4.02	28	3.33	75	3.71	115	2.05	66	1.61		1.93	50
TREE (+Y)	2402	–	2541	–	2454		2487	–	1634	–	2352	–	813	–	403		1039	–
Ir (ppb)	5	2	7	5	12	62	5	21	2	3	2	9	2	11	–		–	–
Os	2	1	4	3	2	6	8	1	3	1	–	–	–	–	–		–	–

Table 3 (continued)

Element	Atlantic Ocean Mean	N	Indian Ocean Mean	N	N. Pacific Prime Zone Mean	N	Non-Prime N. Pacific Mean	N	S. Pacific Mean	N	CA margin Mean	N	CCZ nodules Mean	N	Peru Basin nodules Mean	Indian Ocean nodules[b] Mean	N
Pd	6	2	15	6	4	60	4	23	7	14	4	21	8	12	–	–	–
Pt	567	2	211	6	477	66	228	24	465	15	71	23	128	12	40	–	–
Rh	37	2	20	6	24	65	15	24	33	15	6	23	9	12	–	–	–
Ru	18	2	20	6	18	64	16	24	13	6	10	9	12	12	–	26	–

[a] Dash means no data, unknown, or not applicable.
[b] Indian Ocean nodule data from Jauhari and Pattan (2000), Pattan et al. (2001), Baturin and Dubinchuk (2010), Pattan and Parthiban (2011); Balaram et al. (2006).

3.2. Mechanism of formation

Fe–Mn nodules grow by accumulation of Mn and Fe oxides around a nucleus. Unlike Fe–Mn crusts, nodules acquire metals from two sources, seawater (hydrogenetic) and pore fluids (diagenetic) (Fig. 7). Nodules occur that are solely hydrogenetic (seamounts) or solely diagenetic (Peru Basin), but most nodules are a combination of both. The pore fluids are the predominant source of Ni and Cu, whereas seawater is the dominant source of Co. The pore-fluid metals are derived from early diagenetic redox reactions in upper sediment layers and are incorporated into the Mn-oxide minerals forming in that environment. Nodules produced from oxic diagenesis have the highest Ni, Cu (Halbach et al., 1981), and Li (Hein and Koschinsky, 2013) concentrations. Under suboxic diagenetic conditions, accompanied by high contents of organic carbon, Fe^{2+} ions outcompete Cu^{2+}, Ni^{2+}, and Li^+ for available vacancy sites within the 10 Å manganate that characterizes nodules, thereby decreasing metals of economic interest. The point at which Ni plus Cu increases with oxic diagenetic input and then decreases with suboxic diagenetic input occurs at a Mn/Fe ratio of about 5 (Halbach et al., 1981). Hydrogenetic nodules show strong similarities with hydrogenetic Fe–Mn crusts on seamounts with respect to mechanism of formation (see above) and hence the enrichment of trace metals.

The diagenetic component of most nodules increases their growth rates to about 2 to 50 times faster than those of Fe–Mn crusts, with measured rates of up to 250 mm/Ma (von Stackelberg, 2000). The greater the diagenetic input to nodules, the faster the growth rate. Growth rates of hydrogenetic end-member nodules converge with those of Fe–Mn crusts.

3.3. Mineralogical and chemical compositions

Fe–Mn nodules are composed predominantly of δ-MnO_2 (hydrogenetic), diagenetic 10 Å manganate (todorokite, buserite, asbolan), and less commonly, diagenetic birnessite (Usui and Someya, 1997); lesser amounts of X-ray amorphous iron oxyhydroxide also occur. Minor amounts of detrital aluminosilicate minerals and authigenic minerals such as phillipsite are also present (Piper, 1974). Key physical properties of Fe–Mn nodules are the sheet and tunnel structures of the diagenetic Mn-oxide phases, which allow for the acquisition from sediment pore fluids of large amounts of Ni, Cu, and other elements that stabilize the mineral structure.

In contrast to Fe–Mn crusts, nodules typically have three to six times more Mn than Fe (Table 3). Manganese concentrations can be very high (>30%) in diagenetic nodules, such as the Peru Basin nodules (von Stackelberg, 2000). Traditionally, Ni and Cu have been the metals of greatest economic interest and have mean concentrations in three nodule fields that vary from 1.10% to 1.30% and 0.60 to 1.07%, respectively (Table 3). These percentages will vary somewhat in mine-site-size areas within these major nodule fields. Nodules are also more enriched in Ni, Cu, and Li than crusts, with subequal amounts of Mo, and crusts are more enriched in the other rare metals and the rare-earth elements. The market for Li is growing due to the rapidly increasing use of Li in batteries, including those in electric and hybrid cars. Lithium in CCZ nodules averages 131 ppm and is especially high in diagenetic nodules, averaging 311 ppm in Peru Basin nodules (Hein and Koschinsky, 2013). REEs in nodules are also of economic interest (Spickermann, 2012), but are generally two to six times lower than they are in Fe–Mn crusts, with
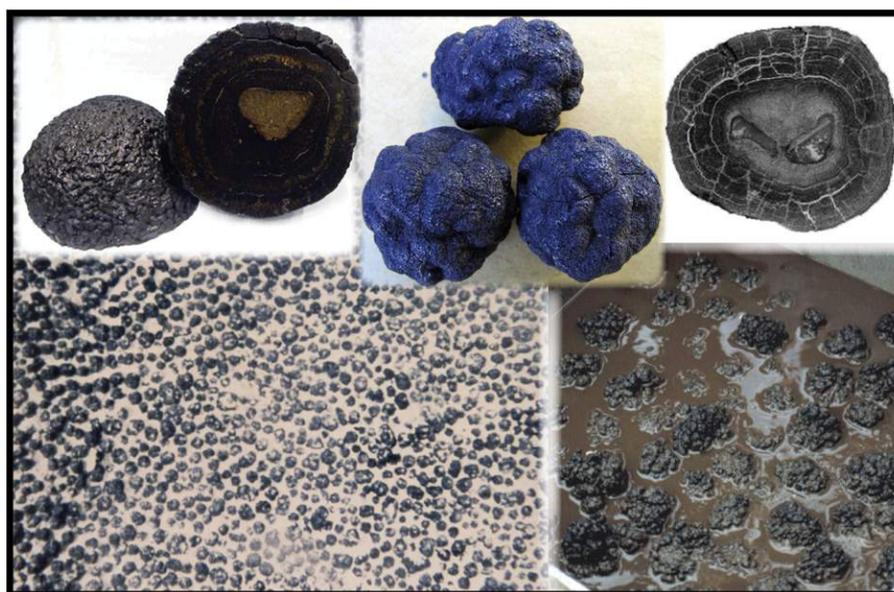

Fig. 5. Clockwise from upper left: cross-section of large 13.6 cm diameter seamount nodule from Lomilik seamount, Marshall Islands EEZ; three abyssal plain nodules each 3 cm in diameter showing a botryoidal surface, from the CCZ; cross-section of nodule collected from the Blake Plateau; diagenetic nodules collected in a box core from the Peru Basin; a dense concentration of nodules in the Johnston Island EEZ, with a field of view of about 4 m by 3 m (1st, 2nd, and 5th are USGS photos, Hein; 4th is photo by Koschinsky).
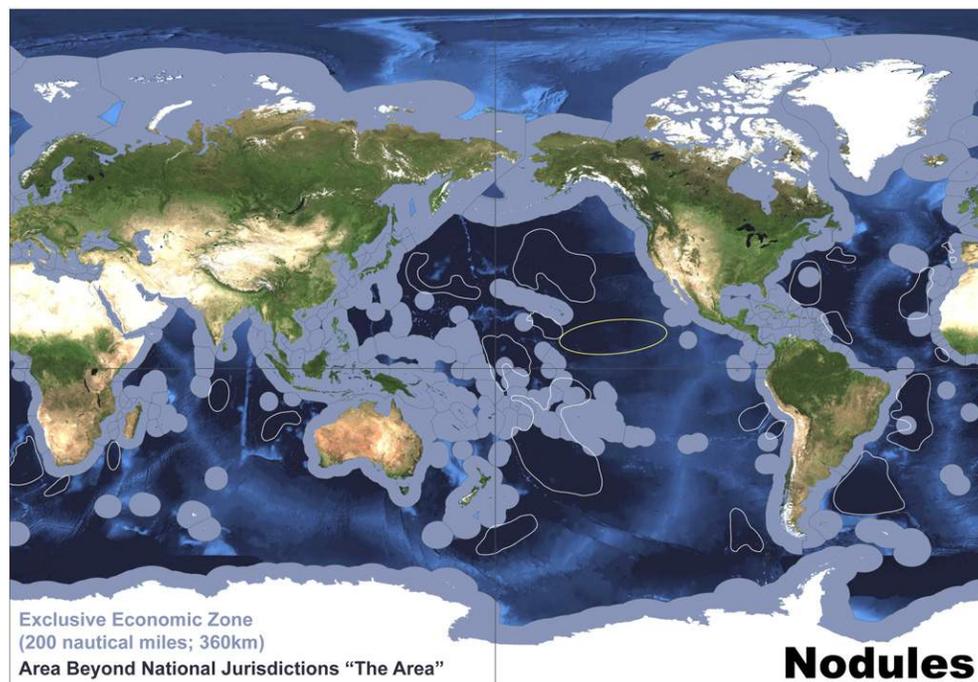
Fig. 6. Map of global distribution of Exclusive Economic Zones (gray shading), areas beyond national jurisdictions (dark black-blue to pale gray-blue), and global permissive areas for development of abyssal plain manganese nodules; the Clarion–Clipperton Zone (CCZ) is the zone of greatest economic interest and is marked by a yellow line; all other areas are marked with a white line; a permissive area does not mean that economic nodule deposits will be found in that area. Small patches of scattered nodules will occur in other areas.

maximum total REEs plus Y in CCZ nodules of about 0.08%. However, there are advantages to recovering REEs even with those low grades, as discussed below (also see Spickermann, 2012). PGEs are generally low in nodules (mean 128 ppb Pt in CCZ nodules) and not of economic interest. Mean concentrations of other metals of interest as potential byproducts of Ni-Cu-Mn mining (Co, Mo, and Zr) are listed in Table 3.

4. Drivers for confronting the challenges of mining deep-ocean minerals

We reached 7 billion people on Earth in November 2011. More than 2.5 billion live in countries with expanding economies and a rapidly growing middle class; an ever-growing number of people live in developing countries that need to build the infrastructure and acquire the resources required to develop a sustainable energy future. The mineral resources required to sustain that growth and to support green- and emerging-technologies can no longer be supplied solely from land-based sources (e.g., Nature Geoscience editorial, 2011; Ragnarsdóttir, 2008). Many of the rare metals required for these green- and high-technology applications are abundant in deep-ocean Fe–Mn crusts and nodules. Further, there are limited sources for many critical metals; China is the major producer for 30 critical metals, including the 14 REEs and Y (Table 2). China's exports of these metals are decreasing as more of their production is being used internally. Decreasing supply and
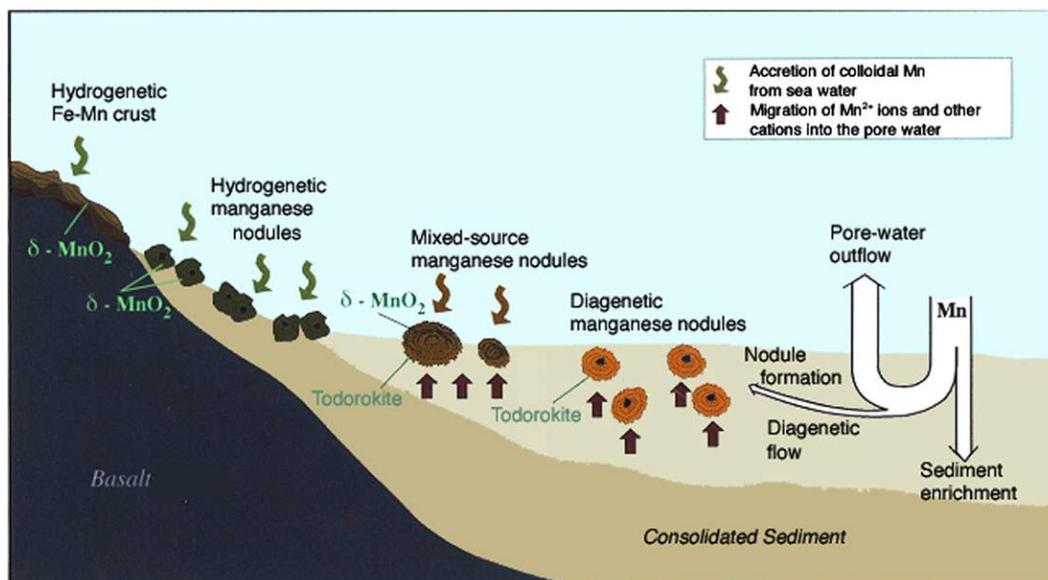

Fig. 7. Diagram of formation of hydrogenetic, diagenetic, and mixed-source Fe–Mn nodules and hydrogenetic Fe–Mn crusts by precipitation from seawater and/or sediment pore water.

increasing demand for metals will open markets to new sources of metals.

The grades of land-based mines are continually decreasing. For example, average Cu ore in 1900 contained 4% Cu, whereas now it is close to 0.5% Cu (Mudd, 2009), with some mines as low as 0.25% Cu. Consequently, more ore must be processed to yield the same amount of metal. In comparison, SMS deposit grades vary from about 1% to 12% Cu (Fig. 8), although the tonnage reserves are unknown. Nodules also contain more than 1.0% Cu and occur in high tonnages. Land-based mines must remove an increasing amount of overburden to reach ore bodies, with super-deep open-pit and mega-underground mines planned. In contrast, marine Fe–Mn crust and nodule deposits are essentially two-dimensional and rest on the seabed with no overburden to remove. SMS are three-dimensional and may be tens of meters thick; the deposits located to date are generally exposed at the seabed with little or no overburden.

REEs found in Fe–Mn crusts and nodules have several advantages over those produced from terrestrial mines. The marine deposits have significantly lower grades, but the tonnages of total REE metals are comparable in the CCZ nodules and PCZ crusts with the largest carbonatite-hosted deposits, Bayan Obo in China and Mountain Pass in California, USA (see below). More important, however, is the much larger complement of heavy HREEs relative to light REEs (LREEs) in the marine deposits. The large terrestrial REE deposits have <1% HREEs, whereas the PCZ crusts and CCZ nodules have respectively, 18% and 26% HREEs of the total REEs (Hein, 2012). This is crucial because the HREEs have the greatest economic value, with yearend 2011 Eu going for nearly $5 million USD per tonne (Bedinger and Bleiwas, 2012; Fig. 9). It should be emphasized that these prices change daily, and Fig. 9 represents an instant in time.

5. Current activities and major players in development of deep-ocean mineral deposits

As of January 2013, exploration contracts have been signed or are pending signature for about 1,843,350 km^2 of seabed (Fig. 10), about half by coastal States for operations within their respective EEZs, and the remainder by the International Seabed Authority in areas beyond national jurisdictions (The Area; Fig. 3). About 45% of the contracted area is for SMS deposits, most within EEZs of SW Pacific States, and only 50,000 km^2 for SMS in The Area. Most of the remaining 55% of the contracts are for Fe–Mn nodules, all in The Area, with two small contract areas for phosphorite, one off New Zealand and one off Namibia, and one very small contract area for metalliferous mud in the Red Sea. These three small sites and one SW Pacific SMS site have been granted mining contracts. In July 2012, the Council and Assembly of the ISA passed regulations for the exploration for Fe–Mn crusts and soon after received two plans of work for contract areas in the west
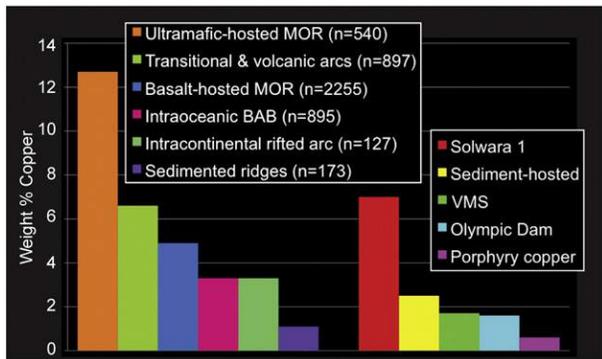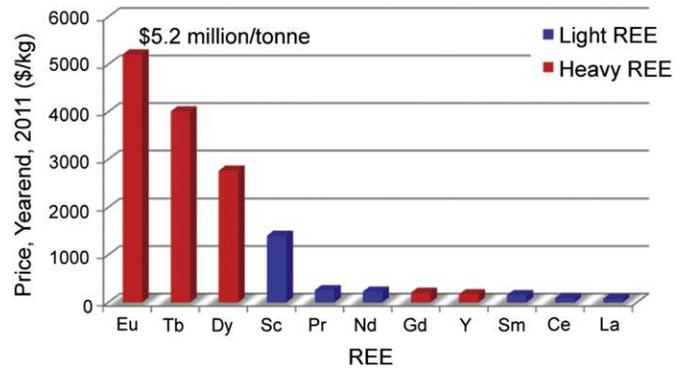

Fig. 9. Select rare earth elements and yttrium prices at yearend 2011. These prices change daily and this figure represents an instant in time.
Data from Bedinger and Bleiwas (2012).

Pacific and one projected to be submitted. We added this 9000 km^2 to the total contract area above (Fig. 10) although those areas will not be officially granted until approved by the Council and Assembly in July 2013 and signed by the ISA and contractors.

The following States, through their Federal agencies, have signed contracts for Fe–Mn nodule areas of about 75,000 km^2 each: China, France, Germany, India, Japan, Korea, Russia, and a group of countries under the name Inter-Ocean Metals (Bulgaria, Cuba, The Czech Republic, Poland, Russia, The Slovak Republic); have signed or pending contracts for SMS of 10,000 km^2 each with China, France, Germany, Korea, and Russia; have plans of work or projected plans of work for Fe–Mn crusts of 3000 km^2 each: China, Japan, and Russia (Table 4). In addition, four companies have contracted or have pending contracts of 75,000 km^2 areas for nodules and one for 58,620 km^2 (Fig. 10). Exploration is accelerating and new requests for contracts are made regularly.

6. Comparisons with land-based reserves

To get a measure of how the metal tonnages of deep-ocean deposits compare with land-based deposits, we use the best-studied area in the global ocean for nodules, the CCZ, and the best-studied area for crusts, the PCZ (Fig. 11; Table 5). Comparisons of total contained tonnages of 15 metals and two metal groups from those two marine areas are made with the global terrestrial reserves (USGS, 2012) and the global terrestrial reserve base (TRB; USGS, 2009), which includes resources that are currently economic (reserves), marginally economic, and subeconomic. The USGS last made TRB calculations in 2009, so those values are used here for comparisons. A conservative estimate of the dry tonnage of nodules in the CCZ is 21,100 million tonnes (ISA, 2010) and for crusts in the PCZ is 7533 million tonnes (Hein and Koschinsky, 2013). CCZ nodule and PCZ crust grades are taken from Table 3.

Nodules in the CCZ have 6000 times more Tl, 1.2 times more Mn, 1.6 times more Te, 1.8 times more Ni, 3.4 times more Co, and 4 times more Y than the entire TRB for those metals. Metals in CCZ nodules as a percent of the TRB are As 88%, Mo 63%, Th 27%, V 25%, Cu 23%, W 21%, Li 20%, Nb 15%, TREO 10%, Ti 7%, and PGM 4%. Peru Basin nodules have the highest Li concentrations, and nodules there contain about 2.7×10^6 tonnes of contained Li, based on a poorly constrained tonnage of nodules of 8.77×10^9 tonnes calculated from data in von Stackelberg (2000); this contained Li tonnage is the same as in the CCZ nodules, but with less than 42% of the total dry tonnage of the CCZ nodules.

With only 36% the tonnage of CCZ nodules, Fe–Mn crusts in the PCZ have just over 1700 times more Tl, 9 times more Te, 3.8 times more Co, 3.4 times more Y, and 1.8 times more As than the TRB. Metals in PCZ crusts as a percent of the total TRB are Bi 46%, Mn 33%, Ni 21%, Mo 18%, V 13%, Nb 13%, TREO 11%, W 11%, Ti 10%, Th 8%, PGMs 5%, and Cu 0.7% (Table 5). These calculations illustrate that significant tonnages of metals occur in the marine deposits, however, it should be kept in

Fig. 8. Left, weight percent of copper in different types of marine SMS deposits (Hannington et al., 2005; Hannington et al., 2010) compared with weight percent of copper from various terrestrial copper deposit types (Match Capitol Resources Corporation, 2011) and a Solwara 1 marine mining operation, right.
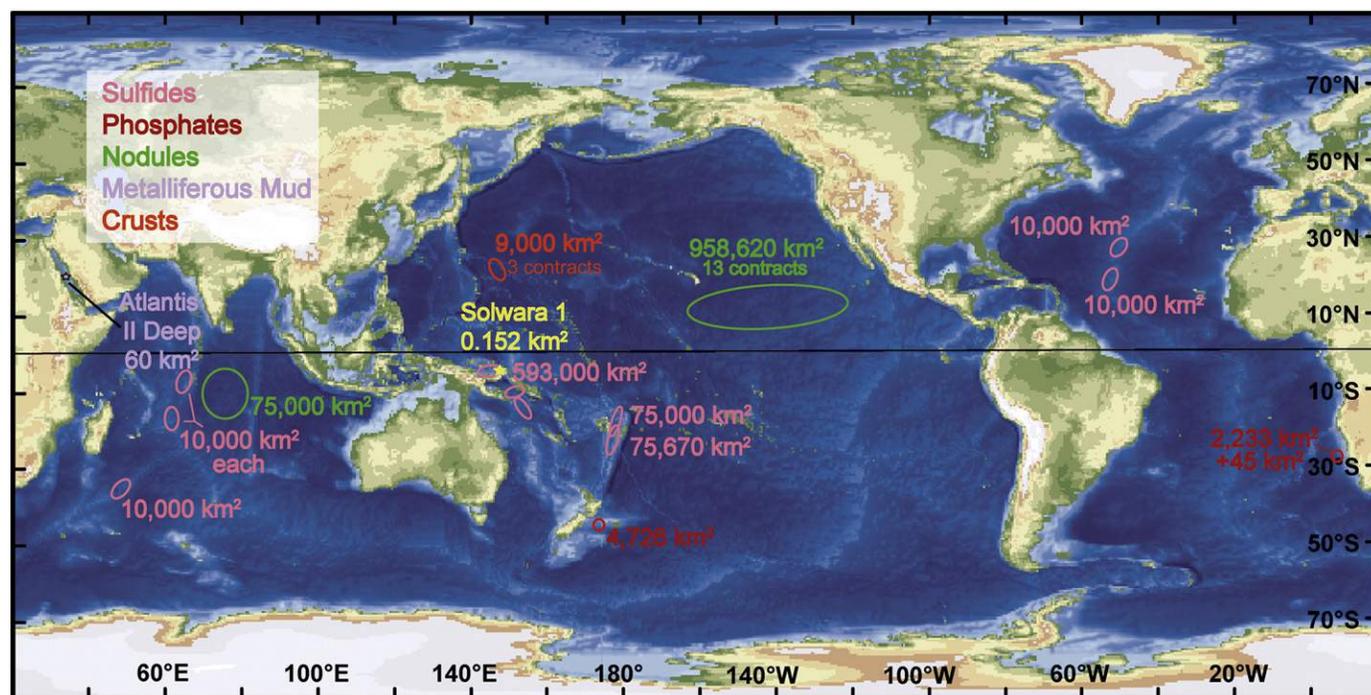
Fig. 10. Map of current deep-ocean mining contracts. Note that some marked areas comprise contracts for multiple countries/agencies; size of ovals not to scale. See text for description of contracts, pending contracts, plans of work, and pending plans of work. About half of the 1,843,354 km² of contracted areas are in EEZs and the other half in The Area. Yellow marks the only mining contract for SMS.

mind that not all the nodules in the CCZ or crusts in the PCZ will be recovered, as is also true for the metals that make up the TRB.

Banakar (2010) presented calculations that compared metal ton-nages in India's 75,000 km² Fe–Mn nodule contract area in the Central Indian Ocean Basin with terrestrial deposits in India for Fe, Mn, Ni, Cu, and Co. He concluded that the terrestrial deposits in India will provide enough Mn for about 150 years of consumption and enough Fe for 300 years. Therefore, the main metals in the nodules are not strategic for India. However, the other metals available in the nodules show a

Table 4
States and companies with deep-ocean minerals contracts.

Entity	Deposit type
States/state agencies	
China	Nodules, sulfides, crusts
France	Nodules, sulfides
Germany	Nodules, sulfides
India	Nodules
Japan	Nodules, crusts
Korea	Nodules, sulfides
Russia	Nodules, sulfides, crusts
Inter-ocean metals	Nodules
(Bulgaria, Cuba, Czech, Poland, Russia, Slovak)	
Companies	
Chatham Rock Ltd.	Phosphate
Namibian Marine Phosphates Ltd. [a]	Phosphate
Diamond Fields International Ltd.[b]	Metalliferous mud
G-TEC Sea Minerals NV	Nodules
Nauru Ocean Resources	Nodules
Tonga Offshore Mining [c]	Nodules
UK Seabed Resources Ltd. [d]	Nodules
Marawa (Kiribati)	Nodules
Nautilus Minerals	Sulfides
Neptune Minerals	Sulfides

[a] Joint venture with UCL Resources Ltd., Mawarid Mining and Tungeni Investments c.c.
[b] Joint venture with Manfa International.
[c] Wholly owned subsidiary of Nautilus Minerals.
[d] Wholly owned subsidiary of Lockheed Martin UK Holdings Ltd.

different story. Domestic supplies for Cu will last only about 30 years, and there is no production of Ni in India although reserves with grades of >0.5% Ni do occur there. Cobalt is produced in India but imports are currently needed to meet demand, which is expected to increase. India's nodule field contains about 7×10^6 tonnes each of Cu and Ni with a grade of about 2% $Cu + Ni$ in the 700×10^6 tonnes of potential ore (Banakar, 2010). The contained metal would meet India's Cu needs for about 25 years and Ni requirements for more than a 1000 years.

Fe–Mn nodules in the Cook Islands EEZ, Central Pacific, are unusually rich in Co, with a mean of about 0.41% Co. About 21×10^6 tonnes of contained Co metal occurs in that nodule field (Hein and Petersen, 2013). A mining operation of 2×10^6 tonnes of nodules per year would provide about 8.4% of the current global production of Co (USGS, 2012).

6.1. Comparisons with Land-based REE Mines

Since the mid 1980s, China and the United States have been the main producers of REEs for the world (Fig. 12). Since about 1991, China has been the dominant producer of REEs and is currently responsible for more than 95% of global production, with the Bayan Obo Mining District as the main contributor and the world's largest REE mine. The U.S. production was from the Mountain Pass mine in California, which closed in 2002, but has now reopened in 2012. Because China is decreasing exports in order to redirect production to internal use, several new REE mines distributed globally are scheduled to begin operations within the next few years.

We compare the reserves for these two largest land-based REE deposits, Bayan Obo (Obo) in China and Mountain Pass (MP) in the U.S. with the REEs in the CCZ nodules and PCZ crusts. The land-based ore deposits are higher grade but lower tonnage ores: MP 0.48×10^8 tonnes at 7.0% total REEs as oxides (TREO) and Obo 8.0×10^8 tonnes at 6% TREO (Berger et al., 2009), compared to the CCZ (211×10^8 tonnes at 0.07% TREO) and PCZ (75.3×10^8 tonnes at 0.21% TREO) (Fig. 13). These grades and tonnages correspond to tonnes of contained TREO of 4.8×10^7 Obo, 0.34×10^7 MP; 1.6×10^7 PCZ, and 1.5×10^7 CCZ. Concen-trations of TREO in the PCZ crusts vary significantly over smaller areas
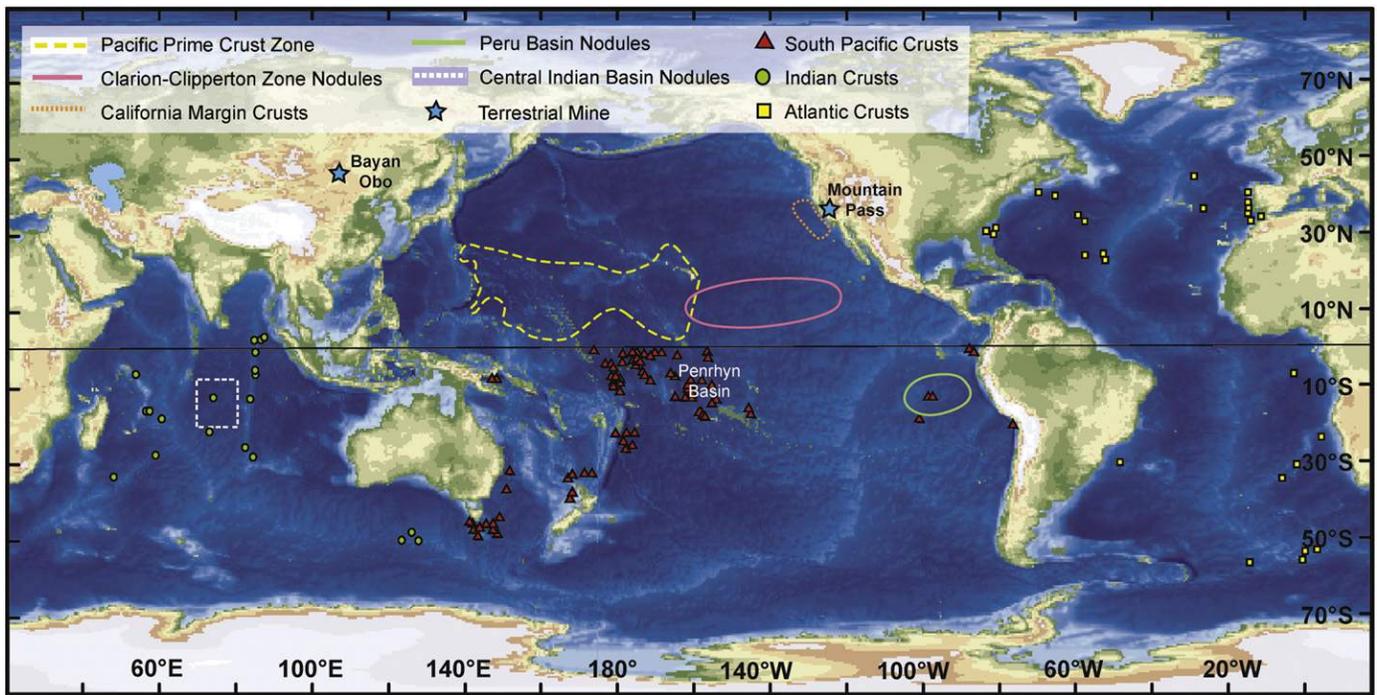
Fig. 11. Map of all well-studied areas for marine mineral deposits, PCZ and CCZ, and the largest land-based rare earth element mines, Bayan Obo in China and Mountain Pass in California, USA; other areas mentioned in the paper and areas on which Table 3 is based.

within the PCZ, with TREO three times (or more) greater than the mean concentration for the entire PCZ; concentrations for smaller areas of the CCZ do not vary to the same extent as they do for crusts.

Of even greater interest than these large tonnages of REEs is the percentage of the TREO that are HREEs because of their much greater economic value. As mentioned above, the land-based deposits have less than 1% HREEs, whereas the CCZ nodules have a mean of 26% HREEs and the PCZ crusts have 18% HREEs. Different researchers include Eu in the

Table 5
Contained metal tonnages ($\times 10^6$ tonnes).[a]

	Clarion-Clipperton Zone Nodules [b]	Global Terrestrial Reserve Base [c]	Global Terrestrial Reserves [c]	Prime Crust Zone [b]
Manganese	5,992	5,200	630	1714
Copper	226	1,000+	690	7.4
Titanium	67	899	414	88
TREO [d]	15	150	110	16
Nickel	274	150	80	32
Vanadium	9.4	38	14	4.8
Molybdenum	12	19	10	3.5
Lithium	2.8	14	13	0.02
Cobalt	44	13	7.5	50
Tungsten	1.3	6.3	3.1	0.67
Niobium	0.46	3.0	3.0	0.40
Arsenic	1.4	1.6	1.0	2.9
Thorium	0.32	1.2	1.2	0.09
Bismuth	0.18	0.7	0.3	0.32
Yttrium	2.0	0.5	0.5	1.7
PGM [e]	0.003	0.08	0.07	0.004
Tellurium	0.08	0.05	0.02	0.45
Thallium	4.2	0.0007	0.0004	1.2

[a] Metals highlighted in red are those with greater tonnages than terrestrial reserves or terrestrial reserve bases.
[b] Nodule tonnage used is 21,100 million dry tonnes and crust tonnage used is 7533 million dry tonnes (from Hein and Koschinsky, 2013).
[c] USGS 2009 reserve base & 2012 reserves (reserve base includes those resources that are currently economic (reserves), marginally economic, and subeconomic).
[d] Total Rare Earth Elements as Oxides.
[e] Total Platinum Group Metals.

LREEs and others in the HREEs. We included Eu in the HREE calculations above, but if included with the LREEs, then the HREE complements would be 25% and 17% respectively.

Several other considerations need to be mentioned while making these comparisons. The first large difference is Th concentrations, which in the land-based deposits is 100 s of ppm compared to the marine deposits, 12 ppm for the PCZ crusts and 15 ppm for the CCZ nodules (Table 3). High concentrations of radioactive Th in the carbonatite ores are of environmental concern with the land-based REE mines and during REE processing. Thorium is hosted in several different minerals in the carbonatites, with monazite having the highest concentrations. On the other hand, extraction of Th as a byproduct of REE production would be an advantage; the demand for Th could increase significantly if Th nuclear power begins to replace U nuclear power; Th plants have many environmental and other advantages over U plants, for example Th has just under 200 times the energy content of U and does not create plutonium, which is used in nuclear weapons, and Th plants have much cleaner wastes (Branan, 2008; see also http://www.popularmechanics.com/science/energy/next-generation/the-truth-about-thorium-and-nuclear-power).

Many of the land-based mines are extracting REEs as the primary ore, whereas REEs in the nodule and crust deposits would be extracted as a byproduct of the focus metals, Mn, Ni, Cu, and Co. Part of the Bayan Obo deposit is mined with REEs as the primary ore and another part with REEs as a byproduct of Fe-ore mining. The cost of mining, transportation, and part of the processing of the marine deposits would be covered by the focus metals, which would leave a residue rich in REEs and other rare metals, including Th. Spickermann (2012) argued that it is this REE concentrate that should be compared with land-based sources and calculated a beneficiation multiplier of 3.25 for this REE-rich concentrate of CCZ nodules. Fe–Mn nodules and crusts can be dissolved with a simple hydrochloric acid leach, thereby releasing the major metals and their sorbed constituents into solution, including the REEs and rare metals. New developments in extractive metallurgy may be able to take advantage of this characteristic of the marine deposits, which is not a characteristic of most land-based deposits.
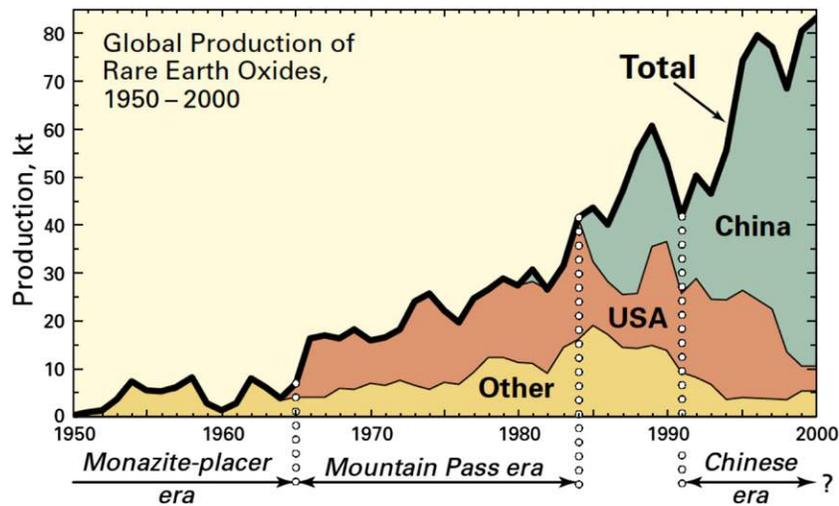
Fig. 12. Global production of rare earth oxides from 1950 to 2000. The Chinese era of production continues to the present day. From Haxel et al. (2002).

7. Unique characteristics for recovery of deep-ocean minerals

Land-based mines leave a substantial footprint of roads, building complexes, and open pits, as well as impacted waterways and millions of tonnes of waste rock; marine-based mine sites will have no roads, seafloor ore-transport systems, or buildings, and little seafloor infrastructure. Fe–Mn crusts and nodules are essentially two-dimensional deposits and exposed at the seabed. SMS deposits have a third dimension of several tens of meters, but have little or no over-burden to be removed. Buried SMS deposits no doubt exist, but little is known about them and exploration has not occurred. In land-based mines, removal of overburden to reach an ore body can be as much as 75% of the material moved. Since the deep-ocean mining platform will be a ship, it can be moved to new locations so that small high-grade deposits can be selectively mined. In addition to the higher grades of the marine deposits, three or more metals can be recovered from a single mine site for each of the three main types of deep-ocean mineral deposits. Deep-ocean marine operations will not impact indigenous or native human populations, an increasing concern with land-based mine sites, although the land-based operations associated with the marine mines might have an impact. Further, no personnel will be in harm's way at the deep-ocean mine site.
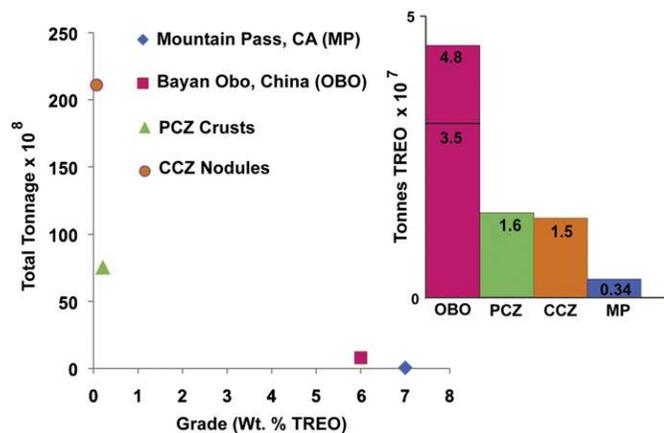
7.1. Environmental considerations

Disturbance of the Earth's surface whether land-based (farming, logging, mining, cities, roads, wind farms, solar farms, etc.) or deep-ocean based (mining, trawling, wind farms, etc.) will disturb or even destroy habitat, so it is essential that the most environmentally sound practices be developed and employed for all Earth-surface activities. Besides the potential environmental advantages of deep-ocean mining listed above, deep-ocean ecosystems generally show low population densities and low diversity compared to areas of many land-based mines, perhaps with the exception of deep-ocean active hydrothermal black smoker vent fields. However, it is not anticipated that those vigorously active systems will be exploited in the near term. Delineation of ecosystem compositions will need to be characterized at each potential mine site, the degree of endemism determined, and an environmental assessment made. An example of an Environmental Code can be found on the website of the International Marine Minerals Society (http://www.immsoc.org). The environmental impact from mineral extraction on the deep-ocean seabed is poorly known; however, a real-world example of an environmental impact statement for its Solwara 1 mine site has been provided by Nautilus Minerals Inc. and posted on the web at Nautilus Cares, n.d (http://www.cares.nautilusminerals.com). Depending on the deposit type and extraction tools, the environmental impacts could be potentially significant and therefore, risk assessments based on in situ experiments at different scales are an essential part of the process (Ahnert and Borowski, 2000).

The potential effects of Fe–Mn nodule mining have been studied during several international programs as described by Hein and Koschinsky (2013). Those programs were based on extensive field studies, as well as theoretical and experimental laboratory studies. It is clear that there will be damage of habitat in the path of a mining vehicle and that a sediment plume of unknown extent will be created in the bottom-water layer. The International Seabed Authority's (ISA, 2008) Kaplan Project concluded that it is difficult to predict the threat of nodule mining to biodiversity and the risk of species decline because of limited knowledge of the numbers and geographic distributions of species. A short-term release of potentially toxic metals from pore waters and desorption from nodule debris may occur, especially if mining decreases the oxygen content in the surface sediment (Koschinsky et al., 2003). Approaches to ameliorate these problems include development of proper mining equipment, use of un-mined corridors and refuges within the ore field so that impacted species can repopulate the area, and mining down current from reference sites with equivalent ecosystems so that larvae would be transported to the mined area.

Fig. 13. Grade versus total tonnage of ore; and inset, resulting tonnes of TREO from two major marine Fe–Mn deposits, PCZ crusts and CCZ nodules (Table 3), as compared to the largest terrestrial REE mines, Byan Obo and Mountain Pass. The two numbers for Obo represent initial reserves and current reserves.

Fe–Mn crust mining would not significantly involve sediment resuspension and would cover an area much smaller than that needed for nodule mining (Hein et al., 2009). Release of metals from abraded metal-rich particles might occur. Crust particles can be effective scavengers of trace metals, which might lead to depletion of some micronutrients, whereas, a release of particles within a well-developed oxygen-minimum zone around seamounts could lead to release of metals. While the risk of chemical contamination is likely to be small, the role of seamounts as hotspots of biodiversity and important breeding grounds needs to be considered (Rowden et al., 2010; Shank, 2010). In this regard, however, a recent analysis indicates that the generalization that seamounts are island habitats with highly endemic faunas that comprise unique communities distinct in species composition from other deep-sea habitats is not supported by the weight of existing data (Rowden et al., 2010).

Deep-ocean ores will be transported to land-based processing plants. Once the ores are transported to existing or newly built processing plants, the same environmental issues that presently exist at such plants will continue; however, newly built plants may be more efficient and employ advancements in green technologies. Processing onboard ship will likely be limited to dewatering of the ore, which would be pumped back down to the water depth of the mine site; in addition, crust mining might use ship-board froth flotation to remove substrate rock collected during crust extraction.

7.2. Technical challenges

There is a large body of literature on potential technologies for the exploration and exploitation of deep-ocean mineral deposits (see Hein et al., 2000 for discussion). However, the first generation technologies for exploitation are available now or are presently being built for the mining of Fe–Mn nodules and SMS, but not for Fe–Mn crusts. Extraction technology for SMS has been adapted from that used in deep-ocean petroleum operations, such as seabed pipe trenching operations, and from offshore placer diamond mining, the latter of which is being adapted from shelf-depth operations to deep-water operations.

Fe–Mn crusts have two major technological hurdles to overcome, one for exploration and mine-site characterization and one for exploitation. It is essential that an exploration tool be developed that is deep-towed or AUV-mounted, and that will measure crust thicknesses (tonnage) in situ. The best avenues may be the development of a multispectral seismic instrument or a gamma-radiation detector, although issues with attenuation of the gamma-ray signal in seawater must be overcome (Hein et al., 2000). Of all the physical properties of a large variety of substrate rock types compared to those of Fe–Mn crusts, gamma-radiation shows the greatest distinction. A second issue is the development of a mining tool that will be able to separate the Fe–Mn crust from the substrate rock on which it is attached without collecting the substrate rock itself, which would significantly dilute the ore grade. This removal must take place on an irregular and often rough seabed at 1500–2500 m water depths, and with crusts attached with variable tenacity depending on the type of substrate rock, which will require significant technological innovations.

8. Future directions

The resource potential of Fe–Mn crusts, nodules, and SMS in the global ocean is not well known, especially for SMS; the CCZ and Central Indian Ocean Basin nodules are the best characterized deposits. However, it is essential that marine mineral deposits be evaluated using methods applied to land-based deposits so that their relative importance can be understood as potential sources of many rare, strategic, and critical metals. Comparative evaluations should include the entire life cycle of the commodities of interest and the environmental justifications for each.

From an engineering standpoint, several important breakthroughs are required for crust mining to become viable, whereas nodule-mining technology is easier and therefore in the final stages of development. The largest impediment to exploration for Fe–Mn crusts is the real-time in situ measurement of crust thicknesses. The largest physical impediment to ore recovery is clean separation of Fe–Mn crust from substrate rock that occurs on an uneven and rough seabed. These technological issues can be aided if the paucity of measurements of physical properties of Fe–Mn crusts and substrate rocks is corrected; a wide-variety of sample types need to be analyzed, especially thick phosphatized crusts. A more difficult challenge is the measurement of physical properties in situ of seawater-saturated samples. These measurements are essential for understanding the mechanisms of sequestration of metals from seawater, contrasting crusts and substrate rocks for the development of exploration technologies, and characterization of crust strength and receptivity to various extraction strategies.

Although significant advances are being made in extractive metallurgy, further advances are needed in the implementation of cost-cutting green technologies. Because all the major and minor metals in crusts and nodules can be put into solution by a simple acid leach, chemical and biochemical processes to selectively recover the metals of interest should be developed, for example the use of specific metal-binding agents. Then the remaining material might be passed on to another extraction operator to recover additional metals of interest if the economic incentive is there—or the strategic need.

Acknowledgments

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