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Prospects for Rare Earth Elements From Marine Minerals

Jim Hein | May 2012

Rare earth elements (REEs) compose the lanthanide group of 15 elements in the periodic table, 14 of which occur in nature and one that does not occur in nature, promethium. Scandium and yttrium are usually considered together with the REEs because of their similar geochemical characteristics. Despite their name, REEs are relatively abundant in the earth's crust. However, because of their geochemical properties, rare earth elements are typically dispersed and not commonly found in concentrated and economically exploitable forms. Their industrial uses in emerging high- and green-technology applications give them an immediate critical and strategic importance.

China currently produces over 95 per cent of the world's REE supply and has recently started to restrict exports, because the REE production is being more directed to domestic use and is being conserved for future use.

The uses of REE in modern societies are extensive and include hybrid and electric cars, wind turbines, weapons systems, motors, magnets for many applications, and a huge market for phosphors in colour televisions and monitors, among many other applications. The automobile manufacturers worldwide cannot operate without the availability of REEs. Within the group of REEs, a number of elements are particularly critical and predicted to be in deficit on the global market by 2014, for example neodymium, europium, terbium and dysprosium (IMCOA, 2011[1] and other sources).

Table 1: Rare Earth Elements

Element	Symbol	Selected Applications
Scandium	Sc	Super alloys, light aerospace components X-ray tubes, catalysts
Yttrium	Y	Ceramics, metal alloys, medical uses, rechargeable batteries, phosphors for TVs high-temperature superconductors
Lanthanum	La	Batteries, optical glass, camera lenses, catalysts for petroleum refining
Cerium	Ce	Catalysts, metal alloys, radiation shielding
Praseodymium	Pr	Magnets, lasers, pigments, cryogenic refrigerant
Neodymium	Nd	High-strength permanent magnets, lasers
Promethium	Pm	Nuclear batteries, guided missiles
Samarium	Sm	High temperature magnets, reactor control rods and neutron shielding, lasers
Europium	Eu	Liquid crystal displays, fluorescent lighting
Gadolinium	Gd	Magnetic resonance imaging contrast agent, memory chips
Terbium	Tb	Green phosphors, lasers, fluorescent lamps, optical computer memories
Dysprosium	Dy	Permanent rare-earths magnets, lasers, catalysts, nuclear reactors
Holmium	Ho	Lasers, nuclear reactors, catalysts
Erbium	Er	Lasers, vanadium steel, infrared absorbing glasses
Thulium	Tm	Portable X-ray machines
Ytterbium	Yb	Infrared lasers, chemical reducing agent, rechargeable batteries
Lutetium	Lu	PET Scan detectors, superconductors, high refractive index glass

This paper was prepared for the International Seabed Authority sensitization seminar held in New York on 16 February 2012 on the work of the ISA and current issues relating to deep seabed mining. Dr. James Hein is a senior scientist with the United States Geological Survey (USGS) in California. He is also an Adjunct Professor of Ocean Sciences at the University of California at Santa Cruz. He has authored or co-authored more than 400 papers and abstracts.

Up until the 1990s, the USA was the main producer of REEs, which came from the Mountain Pass mine in California (*Figure 1*). This mine closed in 2002 as the result of competition from the Chinese Bayan Obo mine, the world's largest REE deposit. Because of the reduction in exports from China, the Mountain Pass mine will reopen in 2013 and several newly developing mines will come on line during the next years, such as in Australia, South Africa, and elsewhere. It may take until about 2016 before new REE sources make up for the reductions in Chinese exports.

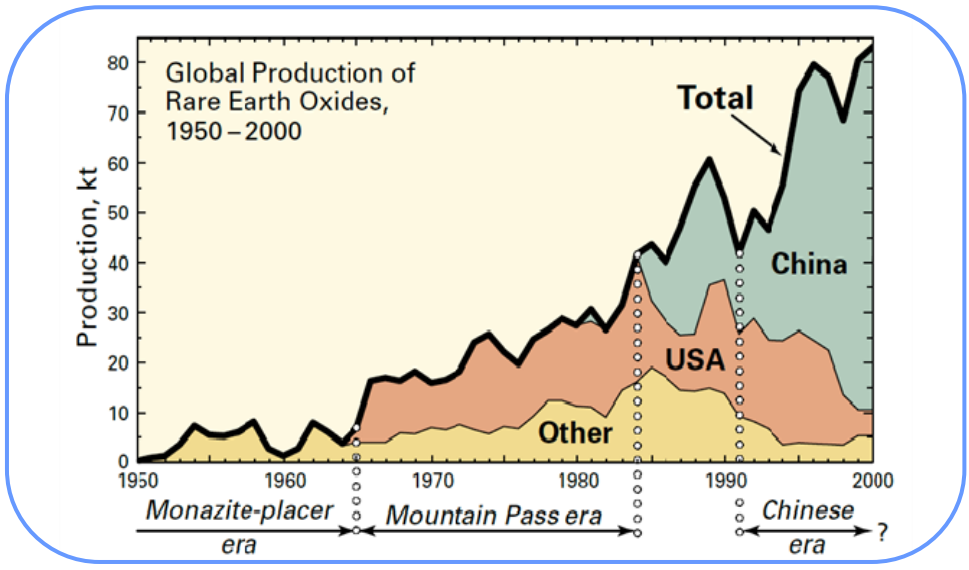


Figure 1: History of rare earth element production (from USGS)

New considerations for the augmentation of REE supplies come from the REEs in the very large tonnage deep-ocean mineral deposits, specifically polymetallic nodules and cobalt-rich crusts. Both deposit types have a significant potential to supply REEs to the marketplace as a byproduct of the extraction of copper, nickel, cobalt, and manganese. Even though the grades (concentration of REEs) of the marine deposits are generally lower than for the land-based deposits, the tonnages are much greater than the land-based deposits. This is true even considering that there are only two prime mineral deposit areas in the Pacific Ocean: The Clarion-Clipperton nodule zone in the NE Pacific in the international seabed area, where nine exploration contracts are presently in force (*Figure 2*); and the prime equatorial Pacific crust zone, which includes both the international seabed area and Exclusive Economic Zones of Pacific Island countries (*Figure 3*).

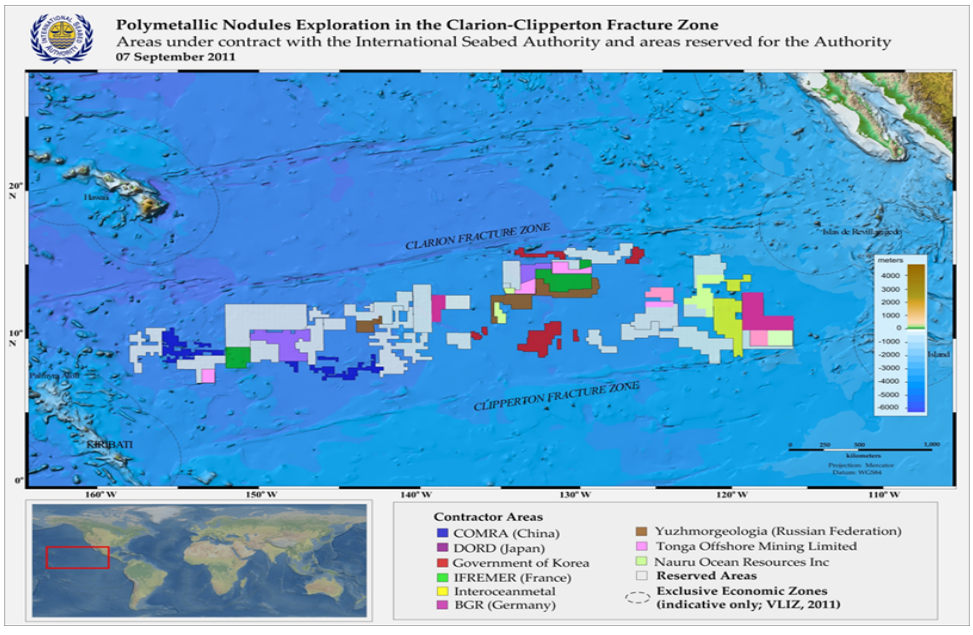


Figure 2: Polymetallic nodules exploration licenses and reserved areas in Clarion-Clipperton Fracture Zone (Map ISA)

Crusts, on average, exhibit about three times higher REE concentrations than nodules and some of the deposits have similar concentrations to the land-based ores in Southern China. It is worthwhile noting that cobalt-rich crusts in the Atlantic and Indian Oceans are expected to be as rich in REE content as in the Pacific, but data and knowledge for those areas remain poor to date.

Polymetallic nodules are small golf-ball sized concretions that sit on the sediment surface on deep-water (4,500-6,500 meters) abyssal plains of the global ocean (*Figure 4*). They are composed predominantly of manganese and iron oxides with much lesser amounts of copper, nickel, cobalt, REEs, lithium, and molybdenum. The main metals are derived from cold ambient seawater and from pore-waters in the sediment. The minor metals are adsorbed onto the major iron and manganese phases. Crusts form pavements on hard-rock substrates on submarine seamounts and ridges throughout the global ocean (*Figure 5*). Those of economic interest occur at water depths of about 1,000-2,500 meters. They are composed predominantly of manganese and iron oxides, cobalt, nickel, REEs, tellurium, molybdenum, zirconium, titanium, bismuth, niobium, platinum, and tungsten. The metals of interest are derived from cold ambient seawater and are adsorbed onto the major iron and manganese phases.

There are several possible advantages to mining the marine deposits in order to augment the production from land-based deposits. The main message is that the economical, geological and environmental factors for land-based and marine deposits need to be evaluated on equal footing.

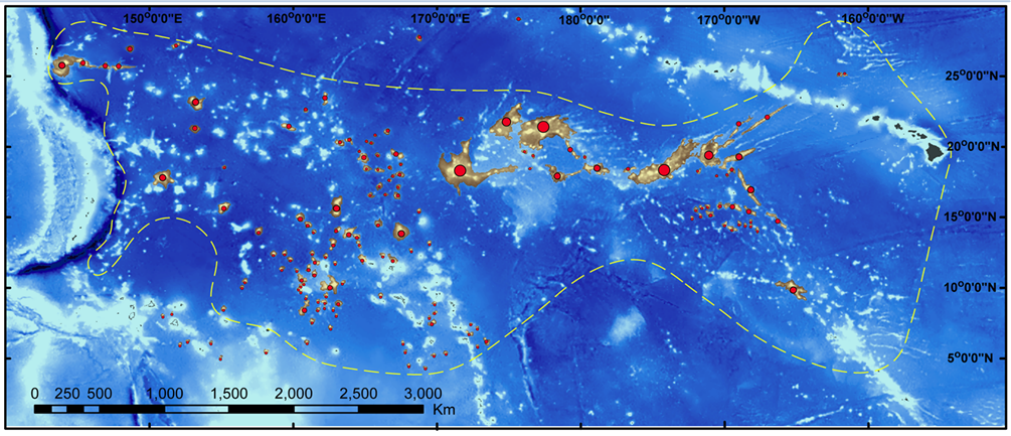
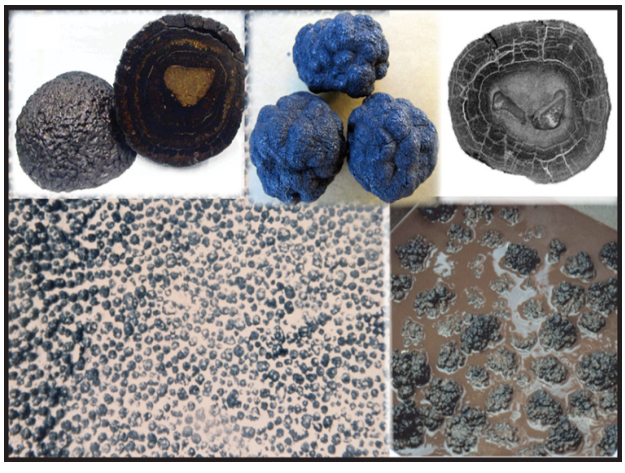


Figure 3:Map of most permissive area for cobalt-rich crusts in the global ocean, located in the western equatorial Pacific (from Hein et al., 2009) [2]

Economically, the relative content of the particularly interesting heavy REEs (HREEs) is higher in seabed deposits than in the largest land-based REE mines, for example the largest REE mine, Bayan Obo (China) and the second largest, Mountain Pass (USA). Both land-based deposits mentioned above contain less than 1% HREEs (percentage of total REE content), whereas the CCZ nodules have a relative content of 26% HREEs and Pacific crusts average more than 18% HREEs. The smaller land-based REE deposits, for example the ion-adsorption clays in Southern China, have similar HREE concentrations as found in the marine deposits.

Comparing the CCZ nodules and Pacific prime crusts with these two largest existing land-based REE mines, the land -based deposits are generally higher in grade but lower in tonnage of ore. However the contained metal (REEs) in the crusts and nodules is comparable to those in the Bayan Obo and Mountain Pass deposits, respectively.



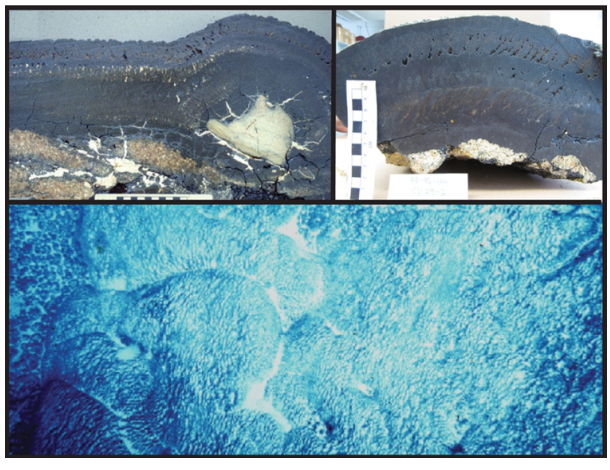


Figure 4: (Left) Polymetallic nodules (from Hein and Koschinsky, 2012)[3]*; Figure 5: (Right) Photo of seabed at 2,000m water depth showing crust pavement (below) and crusts recovered in the Marshall Islands area (from Hein and Koschinsky, 2012)*[3]

An additional advantage of the marine deposits is that it is said to take 1,000 steps to process a land-based ore to isolate one of the HREEs. In contrast, because the REEs are adsorbed onto the main iron and manganese phases, they can be dissolved from seabed ores using relatively simple procedures (dilute acid leach) in a more cost-efficient way.

A third advantage relates to several environmental considerations. The major land-based deposits have high concentrations of toxic waste products (thorium) that need to be carefully managed. A possible advantage of seabed deposits is the absence of such radioactive components in the deposits that significantly increase the technological complexity and costs of REE processing on land. A moveable mining platform for marine deposits allow for the mining of just the high-grade, high-tonnage deposits thereby impacting the least amount of seabed necessary within a crust or nodule zone. Deep-ocean animal population densities are also generally low.

Another environmental advantage is that land-based mines leave a substantial footprint in terms of infrastructure at the mine site, whereas marine deposits do not have seabed infrastructure and only the seabed miner impacts the seabed. Land-based mines commonly require the removal of significant amounts of barren overburden rock, 2-4 times more than the size of the ore body itself. In contrast, marine deposits sit at the seabed with no overburden to remove.

ISA Technical Study

Deep-ocean deposits may offer a partial solution to projected shortages of REEs. In 2011 the Authority commenced work on a technical study designed to address the question of whether sea floor deposits have the potential to become an alternative source of REEs. During the first phase of the project, the geochemical properties of REEs and their geographic variation are being examined in detail. Initially, a global geochemical database of trace metal grades with approximately 2,000 analysed samples, thereof about 700 REE samples has been compiled from various sources, covering the major geographic areas of interest for cobalt-rich crusts and the major polymetallic nodule provinces, including the Central Pacific, the Central Indian Ocean, the Peru Basin, the Penrhyn Basin, the Manihiki Plateau, the Rio Grande Seamounts and other areas of potential interest. The geochemical analyses of metal contents carried out to date in the context of the project are promising, not considering metallurgical factors and processing costs in detail at this stage.

Generally, the extraction of REEs from tailings and interim products may represent a cost-efficient way to produce REEs compared to land-based production, without a negative effect on the production of the main metals because iron is not a target metal; REE by-product operations could turn such residues into profits. An important working hypothesis is that REEs might be particularly enriched in iron-hydroxide bearing tailings and the grades in these tailings may exceed the grades of the REE deposits mined in China. Relevant nodule processing flowsheets with interim products can be found in Halbach et al. (1988)[4] and in Mukhopadhyay et al. (2008)[5].

Endnotes

1. Industrial Minerals Company of Australia. (2011). In: Smith, M. *Rare earth minerals: The indispensable resource for clean energy technologies.*
2. Hein, J.R., T.A. Conrad, and R.E. Dunham. (2009). Seamount characteristics and mine-site model applied to exploration- and mining-lease-block selection for cobalt-rich ferromanganese crusts. *Marine Georesources and Geotechnology, 27 (2), 160-176.*
3. Hein, J.R. and A. Koschinsky. (2012). Deep-ocean ferromanganese crusts and nodules. In Scott, S., (ed.) *The Treatise on Geochemistry*, v. 12. Elsevier (in press).
4. Halbach, P., G. Friedrich and U. von Stackelberg (1988). *The Manganese Nodule Belt of the Pacific Ocean*. Stuttgart: Ferdinant Enke.
5. Mukhopadhyay, R., A.K. Gosh and S.D. Iyer. (2008). *The Indian Ocean Nodule Field: Geology and Resource Potential*. London: Elsevier.

The International Seabed Authority is an autonomous international organization established under the 1982 United Nations Convention on the Law of the Sea and the 1994 Agreement relating to the Implementation of Part XI of the United Nations Convention on the Law of the Sea. The Authority is the organization through which States Parties to the Convention shall, in accordance with the regime for the seabed and ocean floor and subsoil thereof beyond the limits of national jurisdiction (the Area) established in Part XI and the Agreement, organize and control activities in the Area, particularly with a view to administering the resources of the Area.

As part of its mandate to conduct resource assessments of prospective mineral deposits in the Area, the Authority, together with its contractors and scientists, joined forces with a group of technical experts to establish and develop a Geological Model of polymetallic nodule deposits in the Clarion-Clipperton Fracture Zone. The publication (A Geological Model of Polymetallic Nodule Deposits in the Clarion-Clipperton Fracture Zone: ISA Technical Study No. 6) is available online on www.isa.org.jm/files/documents/EN/Pubs/GeoMod-web.pdf.

The Geological Model consists of a set of digital and hard copy maps and tables describing the predicted metal content abundance of deposits in the CCZ, along with associated error estimates. The Prospector's Guide examines all potential proxy data variables identified as important indicators of metal content and abundance, and outlines specific data sets that qualify for use in the Geological Model.

The area of interest for this study is 110°-160° W longitude and 0°-20° North latitude

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