# Rare Earth Elements in the polymetallic nodules – a new challenge

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## ABSTRACT

The Interoceanmetal Joint Organization (IOM) carries out an exploration of laying grounds of polymetallic nodules in the area allotted by the International Seabed Authority (ISA). The most interesting metals in the nodules from the economic point of view have been considered manganese, nickel, copper and cobalt. A big lack of the Rare Earth Elements (REE) is observable on the world metal market in the some past years. The REE are really critical and strategic to the functioning of modern society. Several reports indicated REE as a critical mineral, particularly the EU Report “Critical raw materials for the EU” (2010). Polymetallic nodules are a possible source of the REE. Therefore we are facing a new challenge – to re-evaluate the polymetallic nodules as a possible source of the REE.

KEY WORDS: Interoceanmetal Joint Organization; International Seabed Authority; polymetallic nodules; Rare Earth Elements.

## INTRODUCTION

A principal purpose of this paper is an actual overview, concerning to the possibilities of a utilization of the REE content in the polymetallic nodules, taking an actual demand of the REE into consideration. One of the possible sources of the REE could be the polymetallic nodules, at present explored in the tropical part of the Pacific Ocean (Fracture Zone Clarion - Clipperton) by the IOM and other contractors of the ISA.

## INTEROCEANMETAL JOINT ORGANIZATION AND OTHER CONTRACTORS OF THE INTERNATIONAL SEABED AUTHORITY, THEIR AIMS AND ACTIVITIES

The IOM is one of the pioneer investors in “the Area”, situated in the eastern equatorial Pacific (Fig. 1, ISA webpage). The exploration areas of the other investors (consortia or states) are visible on the Figure 1 too.

“The Area” is administrated by the ISA, 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 ISA 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.

The ISA, which has its headquarters in Kingston, Jamaica, came into existence on 16 November 1994, upon the entry into force of the 1982 Convention. The ISA became fully operational as an autonomous international organization in June 1996 (ISA webpage).

For the IOM and other investors in the Area a first principal task was to carry out an exploration of laying grounds of polymetallic nodules (Franzen, 2011). The most interesting metals in the nodules from the economic point of view have been considered manganese, nickel, copper and cobalt. A problem of the REE was analyzed in the IOM last time by Kotlinski, Parizek and Rezek (1997).

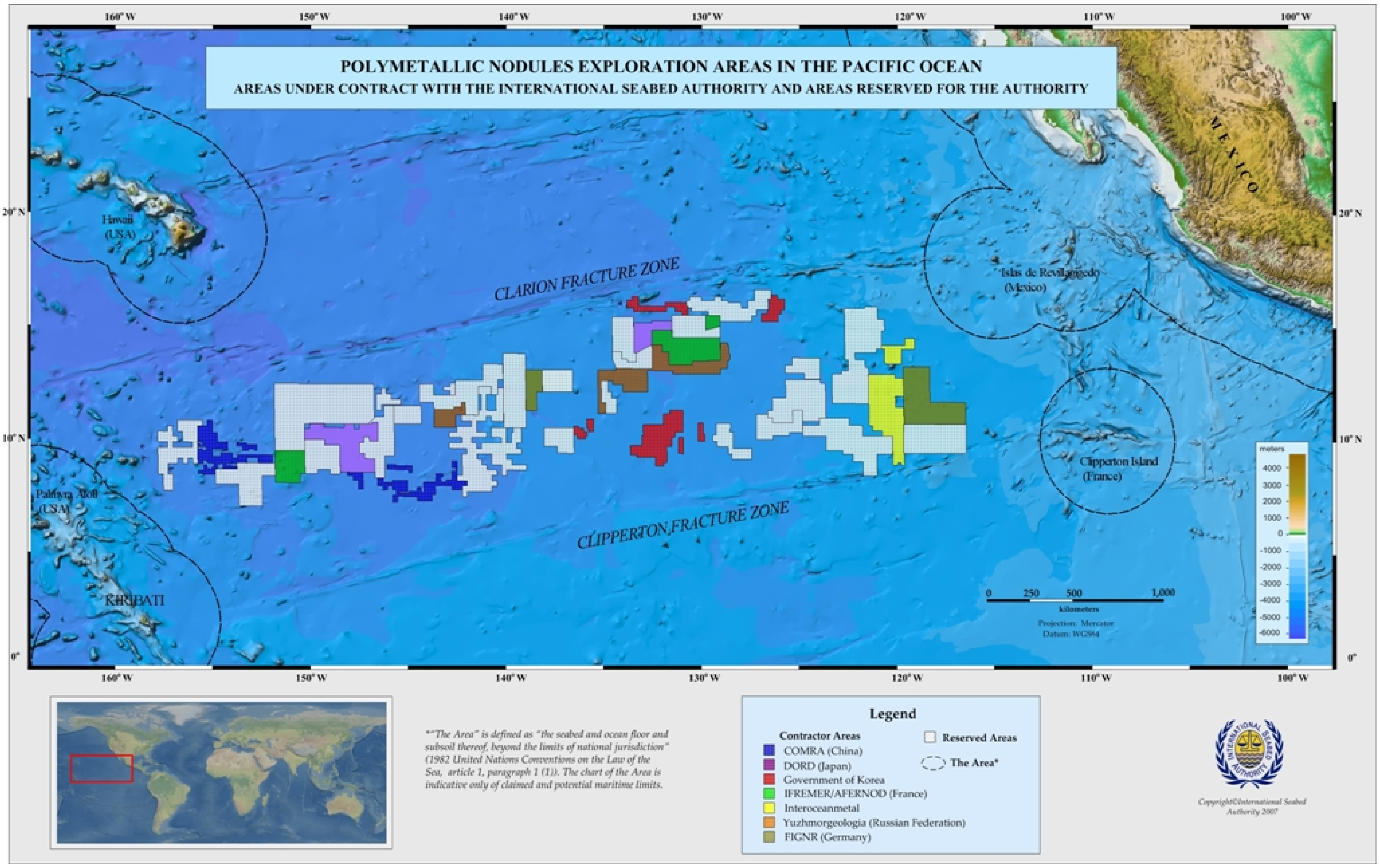


Fig. 1 Exploration areas in the Pacific Ocean

## RARE EARTH ELEMENTS AS THE STRATEGIC AND CRITICAL MINERALS

Rare earths are relatively abundant in the Earth's crust, but discovered minable concentrations are less common than for most other ores. World resources are contained primarily in bastnäsite and monazite. Largest reserves are discovered in China which is world's dominant REE producer at present. Undiscovered resources are thought to be very large relative to expected demand (USGS Mineral Commodity Summaries, 2011). REE are used in wide range of applications (chemical catalysts, metallurgical applications and alloys, petroleum refining catalysts, automotive catalytic converters, glass polishing and ceramics, rare-earth phosphors for computer monitors, lighting, radar, televisions, and x-ray-intensifying film, permanent magnets, electronics, laser crystals, industrial cutting and welding, nonlinear optics, photochemistry, high-temperature superconductors and other). Many REE applications are highly specific and substitutes are inferior or unknown.

The REE are really critical and strategic to the functioning of modern society. Several reports indicated REE as critical mineral, particularly the EU report *Critical raw materials for the EU* (2010). The EU Commission on Enterprise and Industry has received its June 2010 report from the Raw Materials Supply Group, which draw up a list of critical materials. It defines the "high tech" metals and minerals (including REE) having significant economic importance for key sectors, high supply risks and a lack of substitutes. As shown, rare earth elements are materials of highest supply risk for Europe (Fig. 2). The report highlights the problem: Of greater relevant are changes in the geopolitical-economic framework that impact on the supply and demand of raw materials. These changes relate to the growing demand for raw materials, which in turn is driven by the growth of developing economies and new emerging technologies.

Other documents indicating the REE criticality are the US DOE (Department of Energy) report *Critical Materials Strategy* (2010), focused on materials used in clean energy technologies and *Securing Materials for Emerging Technologies* (2011) report by the APS (American Physical Society) and the MRS (Materials Research Society), describing chemical elements critical to energy related technologies.

Moreover, the event of China's REE embargo on Japan in 2010 was a big wake-cup call making governments see that the REE and all other minerals, where any country has dominance, are open for use as bargaining chips.

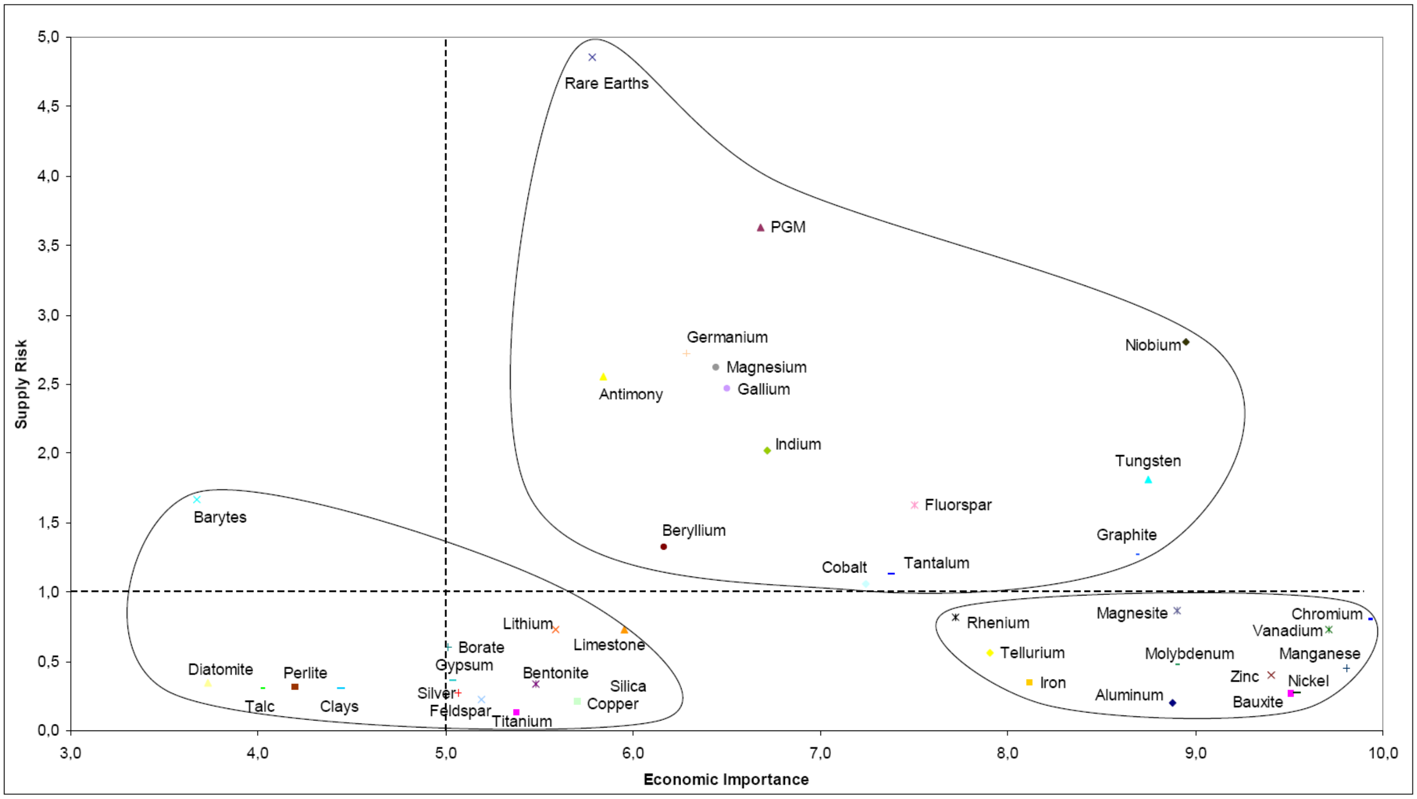


Fig.2 Critical materials for EU according to supply risk and economic importance (European Commission, Enterprise and Industry, 2010)

## REE IN POLYMETALLIC NODULES

Polymetallic nodules (PNs) are complex heterogenic systems based on inorganic phase (especially manganese and iron oxides) and organic phase too (fragments of phosphatic character). Mineral composition is represented by todorokite, asbolane-buserite, birnessite, vernadite (Mn oxides) and goethite (Fe oxide).

Although the interest for nodules started because of their manganese, nickel, copper and cobalt contents, further analyses reveals the presence of other raw materials, including REE. Analyzed nodule samples taken from the IOM exploration area show enhancement in the REE total abundance (Tab. 1), REE content varies from 302 to 2 020 ppm, especially Ce (80-940 ppm), La (100-450 ppm) and Nd (80-340 ppm). Generally the subgroup elements of light lanthanoides (cerium subgroup) have majority in composition, while yttrium subgroup elements show smaller values (Kotlinski et al., 1997). REE distribution in nodules of different genetic types is in Tab. 2. The genetic types of nodules differ in morphological features, mineralogical composition and chemical content. From correlation relationships result that REE have most of all a structure of matter on Fe oxides. Kotlinski et al. (1997) estimated that REE are fixed to nonmetalliferous accessoric minerals (barite, mica, feldspar and other).

Table 1. REE distribution in PNs in area investigated by IOM (Kotlinski et al., 1997)

| Element | number of samples | min. (ppm) | max. (ppm) | mean (ppm) | standard deviation |
|---|---|---|---|---|---|
| La | 158 | 100 | 460 | 227.3 | 56.5 |
| Ce | 158 | 80 | 940 | 392.7 | 120.3 |
| Nd | 158 | 80 | 340 | 217.3 | 38.8 |
| Sm | 161 | 17 | 67 | 35.3 | 8.2 |
| Eu | 62 | 1 | 22 | 10.6 | 3.3 |
| Gd | 27 | 16 | 113 | 48.9 | 21.3 |
| Tb | 113 | 0.8 | 10.3 | 3.6 | 1.9 |
| Ho | 27 | 3.7 | 31.5 | 7.5 | 5 |
| Tm | 27 | 1.5 | 5.7 | 3 | 1.1 |
| Yb | 113 | 1.9 | 17.4 | 6.9 | 2.6 |
| Lu | 113 | 0.4 | 3.2 | 1.4 | 0.5 |

Table 2. REE distribution in PNs genetic types in area investigated by IOM (Kotlinski et al., 1997)

| Element | H | | HD | | D | |
|---|---|---|---|---|---|---|
| | n | avg. (ppm) | n | avg. (ppm) | n | avg. (ppm) |
| La | 46 | 271.5 | 22 | 209.5 | 70 | 195 |
| Ce | 46 | 484.3 | 22 | 361.4 | 70 | 334.1 |
| Nd | 46 | 239.5 | 22 | 207.3 | 70 | 207.1 |
| Sm | 46 | 43.1 | 22 | 32.9 | 73 | 32 |
| Eu | 15 | 11.5 | 10 | 9.7 | 28 | 10.5 |
| Tb | 17 | 5.2 | 18 | 3.1 | 58 | 3.3 |
| Yb | 17 | 8.8 | 18 | 6 | 58 | 4.5 |
| Lu | 17 | 1.6 | 18 | 1.2 | 58 | 1.4 |

n – number of samples
H – hydrogenetic type nodules
HD – hydrodiagenetic type nodules
D – diagenetic type nodules

New results (2010) of 8 PNs analyses for REE content performed in Trondheim, Norway are presented in Tab. 3.

Table 3. Analyses of REE distribution in PNs in area investigated by IOM – totally 8 samples analyzed (2010)

| Element | min. (μg/g) | max. (μg/g) | average (μg/g) |
|---|---|---|---|
| Y | 58.14 | 79.09 | 67.06 |
| Sc | 6.78 | 9.94 | 8.39 |
| La | 77.92 | 100.33 | 89.85 |
| Ce | 139.58 | 177.36 | 163.33 |
| Pr | 19.88 | 26.01 | 23.39 |
| Nd | 96.37 | 125.66 | 113.25 |
| Sm | 22.37 | 28.36 | 25.97 |
| Tb | 3.72 | 4.75 | 4.31 |
| Dy | 11.76 | 15.91 | 13.89 |
| Ho | 3.61 | 4.69 | 4.15 |
| Er | 10.04 | 13.57 | 11.82 |
| Tm | 1.31 | 1.76 | 1.52 |
| Yb | 9.04 | 11.24 | 10.23 |
| Lu | 1.26 | 1.63 | 1.44 |

Latest analyses for REE content in polymetallic nodules (Tab. 4) was realized in Geoanalytical Laboratories of State Geological Institute of Dionyz Stur. Two archive samples from former exploration expeditions, 2001 and 2009 were analyzed for wide scale of chemical elements. Concentration of particular rare earth elements is relative to concentration of ferrum (Fe) and manganese (Mn). We can conclude that rare earth elements are precipitated from aqueous medium together with iron and manganese oxides.

Table 4. Selected analyses of REE distribution in PNs in area investigated by IOM – 2 samples (2011)

| Element | PMK 1 (mg/kg) | PMK 2 (mg/kg) |
|---|---|---|
| Y | 80 | 60 |
| Dy | 63.1 | 18 |
| Er | 9.57 | 6.30 |
| Eu | 6.38 | 3.58 |
| Gd | 24.2 | 14.9 |
| Ho | 3.78 | 2.34 |
| Lu | 1.35 | 0.95 |
| Nd | 104 | 62.8 |
| Pr | 25.1 | 14.7 |
| Sm | 23.9 | 14.0 |
| Tb | 4.42 | 2.33 |
| Tm | 1.80 | 1.21 |
| Yb | 9.61 | 6.15 |
| La | 89 | 50 |
| Ce | 332 | 156 |

PMK 1 – IOM area, depth 4.4 km, localization 120 °W, 10 °30´N
PMK 2 – IOM area, localization 119°35´W 11°N

## CONCLUSIONS

For Europe and other developed economics in the world rare earth elements are materials essential for the high-tech production. At present, REE are materials of highest supply risk. Polymetallic nodules of deep sea deposits may become one of other non-conventional sources of rare earths.

REE content and distribution in polymetallic nodules is variable depending on several factors and conditions, including bearing depth, mineralogical composition, geochemical background, etc. REE content in polymetallic nodules confirmed positive cerium (Ce) anomaly also in recent analyses. Content of REE in PNs in comparison with classical deposits of REE raw materials is generally lower. According to complex utilization of polymetallic nodules potential, there is also potential of using rare earths (as by-product). This REE content is comparable with content of REE in industrial scrap, waste and other secondary sources of rare earths (Kotlinski et al., 1997). Utilization of REE from polymetallic nodules is conditional according the mineral processing method, to secure extraction of all mercable elements. In IOM, solving of technology process was primarily aimed to separation of major metals (manganese, nickel, copper and cobalt). Possibility of REE utilization is new challenge and way to increase future production and processing efficiency of PNs marine mining.

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