NEAR FUTURE REE RESOURCES FOR EUROPE- THE NEW FRONTIER OF MARINE EXPLORATION, MINING AND PROCESSING

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Abstract

The Marine exploration and mining is a reality. It is now well established the importance of some shallow and deep sea mineral formations as a new and near future source for REE. The shallow marine water exploration and mining for placer deposits, including REE, is already an important ongoing activity in the Continental shelf in many places around the world. In Greece and especially in some areas of the continental shelf of the N.Aeqean, an extensive heavy mineral mineralization occurs rich in Allanite, being responsible for the high content in REE (mainly lights) Th, U. In parallel the deep sea minerals exploration proved that there is also a distinct REE type of mineralisation associated with deep sea polymetallic nodules and cobalt rich crusts. These formations represent an important future resource, since they not only contain base metals such as Mn, Ni, Co, Cu and Zn, but are also enriched in critical or rare high-technology elements such as Li, Mo, Nb, W, the rare earth elements and yttrium (REY). Both types have a significant potential to supply REEs to the marketplace as a byproduct of the extraction of Mn, Ni, Cu and Co, in the near future. The economo-technical assessments, showed that finally the "basket value" of any REE that can be recovered from these formations, is likely to be higher than those of terrestrial deposits, due to the relatively high portions of Nd, Pr and heavy rare earths (especially Dy).

Marine REE resources: exploration and mining perspectives

Introduction

The global economic development and the fast growth rate of the population of our planet creates a great need to find new resources. During 2011 the humanity reached 7,000,000,000 People! Only 2.5 billion live in countries with booming economies and a rapidly growing middle class i.e China and India. This increase is already creating even more pressure on global and non-renewable mineral resources. So the exploration and exploitation of mineral resources of sub-sea must become a reality in this century that we already.

Europe especially faces a booming problem: The increasing imbalance between domestic production and needs especially in non renewable natural resources. And the question is: Where will the resources come from to sustain that growth, and to support green and emerging technologies? The significant dependency, particularly of Europe from imported strategic and critical mineral raw materials is now a painful reality.

Inevitably in the non long feature the marine mineral resources will provide additional safeguards for our needs in mineral resources.

The oceans are an important resource for mankind if and still need to be explored quite until used in their full potential. Oceans and seas associated with them form a continuous area covering three-quarters of the Earth's surface. Within this sphere, we have the sources of minerals and energy that is largely untapped. It is noteworthy to know that the world's continental shelf and the continental margins are larger in area than the Moon and offer an almost pristine area for exploration.

The Marine exploration and mining is now a reality. The shallow water mining is a dynamic activity since many years ago, dealing mainly with aggregates, precious stones (diamonds, gems) and placer deposits. On the other hand, the deep sea exploration is now an extensive activity and many companies as well as state organizations are investing a lot of capital on it. The results and the progress especially during the last 10 years is more than impressive. In the next few months the first deep sea mine will be a reality on the EEZ of the Papua New Guinea.

It is now well established the importance of some shallow and deep sea mineral formations as a new source for REE. The shallow marine water exploration and mining for placer deposits (light heavy minerals) is already an important ongoing activity in the Continental shelf of Easter Africa and Sri Lanka, South East Asia, Australia.

In parallel the extensive deep sea exploration proved important mineral resources for REE mainly deep sea Mn nodules and Co rich crusts .

The Shallow Water Exploration and Mining-The Placer Deposits

The placer deposits containing minerals rich in REE (i.e Monazite, Allanite) belongs to the so-called light heavy minerals (specific gravity 2.8-6.1).

They occur mainly in beaches, modern or drowned, and in the immediate offshore area. (Table 1). The South East Asia contains some important light heavy mineral deposits, particularly off India and Sri Lanka.

Placer deposits containing titanium, thorium, rare earth elements and zirconium have been mined at a location on the southeast coast of Sri Lanka. (Fig. 1a)

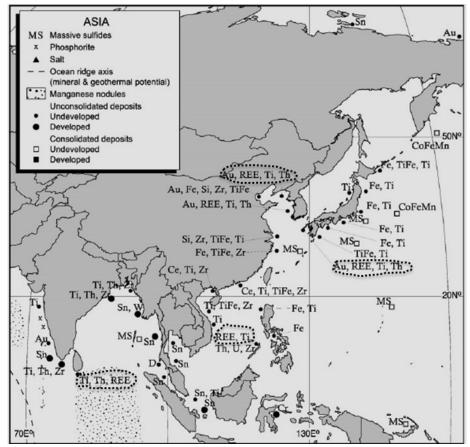


Figure 11a. Offshore placer mineral of Asia-The REE mineralization is outlined ¹

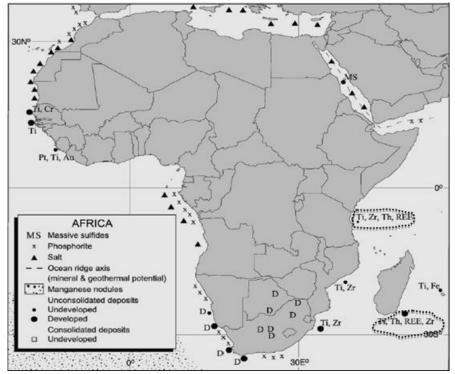


Figure 1b.Offshore placer minerals of Africa (1)-The REE mineralization is outlined

The Corridor Sands (1765 million tonnes containing 73 million tonnes of ilmenite at an estimated average ilmenite grade of 4.14%; Mining Review Africa, 2003) and the Moma disseminated beach deposits (estimated 60 million tonnes of ilmenite; Planet Ark, 2003) onshore near the coast of Mozambique are both under development and are considered, respectively, the world's largest and second largest undeveloped resources of titanium dioxide (TiO₂). Numerous undeveloped placer deposits of light heavy minerals (ilmenite, rutile, magnetite, zircon, garnet, and monazite) are present on beaches and offshorethe Indian sub-continent (Roonwal, 1986; Rajamanickam, 2000) and P. R. China Institute of Marine Geology, 1988; Tan et.al 1996)

Table 1. The main placer developed marine mineral deposits enriched in critical and especially in REE worldwide $(^{1,2})$

Name (Latitude, longitude)	Commodity	Type of deposit	Water depth <m)< th=""><th>Location</th></m)<>	Location
Richard's Bay 28.8°S, 32.0°E	Titanium, zirconium	Placer	0-30	South Africa
Fort Dauphin	Titanium, thorium, REE	Placer	0	Sri Lnca
25.0°S, 47.0°E	Zirconium			
Kanniyaknmari	Titanium, zirconium, thorium	Placer	0	India
Manavalakurichi 8.2°N, 78.5°E				
Chatrapur	Titanium, zirconium,	Placer	0	India
19.4°N, 85.0°E Castle Island	Barium	Consolidated layered	0-5	Alaska, USA

Heavy minerals mineralisation in the littoral zone and the continental shelf of the N. Aegean Sea-Greece

The first research project in the shore-line and in the upper continental self, by the Greek Geological Survey (IGME), in the N. Aegean Sea took place in mid-80's. It was an extensive marine geological and geochemical research programme on the Strymonikos plateau off eastern Macedonia, in N. Greece (Figure 2).

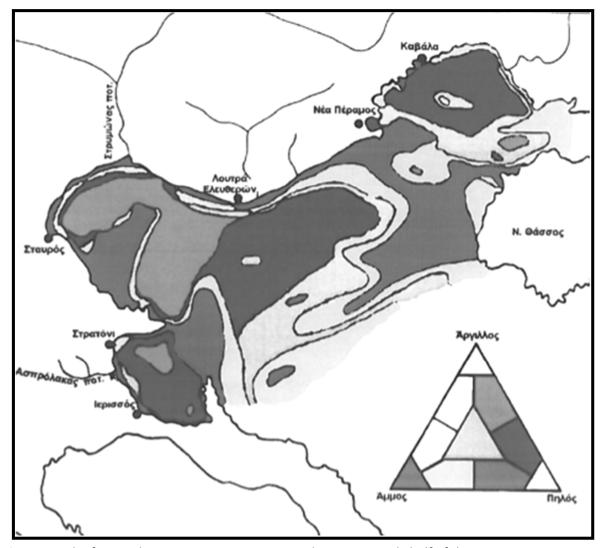


Figure 12. The first exploration programme area in the Continental Shelf of the N.Aegean Sea-Greece 3

During this program the surface sediments were examined in order to locate possible placer deposits in the area. The results were very encouraging and during 1996, the Greek Geological Survey launched a detailed exploration project with the title "Evaluation study of the Marine heavy minerals mineralisation rich in Th-U and REE", aiming to investigate the qualitative and quantitative parameters of polymetallic heavy minerals mineralisation in the Strymon Gulf. (Figure 2).

The outcome of this project was summarised in an excellent publication by the Greek Geological Survey(IGME) with the **title "Evaluation study of the Marine heavy minerals mineralisation rich in Th-U and REE"** by F.Pergamalis, S.Papachristopoulos, D.Karageorgiou and A.Koukoulis published in 2001.^{4,5} Below are presented the most important findings and conclusions of this publication:

In the Bay of Strymon (Orphanou) there is an extensive polymetallic heavy minerals mineralisation rich in titanium, rare earths, thorium, uranium and traces of gold in the

form of sandy formation. The total estimated resources (coastal and underwater) were estimated to 490 x 10 6 tn, with an average REE content about 1.17%. 4

- This sandy formation rich in heavy minerals shows high content of Allanite estimated at an average value of 2.39%.
- ❖ The allanite is mainly responsible for the high content in REE (mainly lights), Th, U, etc. For three analyzed oxides the REO La₂O₃, Ce₂O₃ and Nd₂O₃, revealed contents from 10.3 to 15%, whilst in the representative sandy ore sample was 0.007%. The proportions of Ce₂O₃/La₂O₃ have a variation between 1.42 to 2.27 for the respective proportions of the original representative ore sample. (J.Katsikis Greek Geological Survey)
- The sandy heavy mineral concentration are rich in Th (1283 to 1710 ppm) enriched in Nb (200ppm), Y (150ppm)
- The initial heavy mineral concentrations in the sand fractions exhibit high concentrations in light REE (La to Sm) over 7000 and 11000ppm respectively, which represents about 95% of the total content in REE.
- ❖ The highest concentrations follow the order of: Ce, La, Nb and Pr representing around 93% of those in proportions from 52 to 65%, 20-27%, 11-16% and 4-5% respectively for the above REE
- Therefore the initial placer mineralisation practicality approaches a "rare earths ore" similar to the concentrate (mischmetal of, La, Nb,Pr, which seems to have a good value in respect concentrates marketed for La, Nb and Ce, La. 4,5

Based on the above *very encouraging results, in his narrow area, and taking into consideration the* great strategic and geopolitical importance of REE, the Greek Geological Survey (IGME), started a new systematic exploration programme, with a budget of about €2,000,000.00, throughout the whole continental shelf of the North Aegean, in order to find out if i) these important concentrations of REE exhibit the same qualitative and qualitative characteristics i.e if the resources can be converted to reserves, and ii) if they present an economic target under the present economic technical conditions. In this exploration programme which already started a few months ago IGME collaborates with the Greek National Oceanographic Institute (HCMR).

The Deep Sea Exploration and Mining

Recently and after the vast progress in deep sea exploration and deep sea technology it is quite evident that the deep sea mineral resources can be a very important and vital new supply of mineral commodities for the humanity.

Examining especially the perspectives of mining deep sea deposits for REE deposits we can divide them into categories:

- 1. Longer-term perspectives
- 2. Near future term perspectives

A. The longer-term perspectives-The Deep-sea mud, especially in the Pacific Ocean as a potential resource for rare-earth elements

(Y.Kato et.al. 2011) ⁶ have discovered a new type of mineral resource, named REY (rare earth elements and yttrium)-rich mud, distributed in vast quantities throughout a large part of the Pacific Ocean.

REY-rich mud containing up to approximately 0.2 percent by weight total REY occurs across the central north and southeastern Pacific Ocean in average thicknesses of approximately 24 m and 8 m, respectively.

Their data showed that REY stored in these Pacific mud deposits amounts to a possible resource 10^2 to 10^3 times greater than the world's current land reserves of 110×10^6 tonnes of REY oxides, depending on local stratigraphic continuity and thickness of the REY-rich mud. Uptake by materials such as hydrothermal Fe-oxyhydroxides and phillipsite seems to be responsible for the high REY content, and consequently REY are readily recovered by simple acid leaching and are a suitable resource for developmentas their first experimental tests proved.

The newly discovered REY-rich mud may constitute a highly promising source of rare earth elements in the long future since a lot of exploration work and beneficiation tests are necessary.

B. The short term prespectives-The special case of the deep sea polymetallic nodules and cobalt rich crusts

Undoubtedly the exponential advances on exploration, exploitation, beneficiation techniques as well as mining technology concerning deep sea mineral resources, proved that except the REY (rare earth elements and yttrium)-rich deep sea mud, as it has been described above, there is also a distinct REE type of mineralisation associated with deep sea polymetallic nodules and cobalt rich crusts. Both types of mineralisations are primary i.e many nodule deposits show both a diagenetic and a hydrogenetic compound due to accumulation of metals both from pore water and from seawater. These nodules are known as mixed-typed nodules and are characteristic for the abyssal plains e.g. within the Clarion Clipperton Zone (CCZ) in the Central Pacific. Ferromanganese crusts and nodules represent an important future resource, since they not only contain base metals such as Mn, Ni, Co, Cu and Zn, but are also enriched in critical or rare high-technology elements such as Li, Mo, Nb, W, the rare earth elements and yttrium (REY). Both types have a significant potential to supply REEs to the marketplace as a byproduct of the extraction of copper, nickel, cobalt, and manganese. 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. According to Hein(2012), ^{7,8} it is quite possible that cobaltrich crusts in the Atlantic and Indian Ocean are expected to be as rich as in REE content as in the Pacific, but data and knowledge for those areas remain poor to date. These metals could be extracted from nodules and crusts as a by-product to the base metal production. However, the most proper separation techniques available that selectively extract certain metals out of the carrier phases, are under investigation.

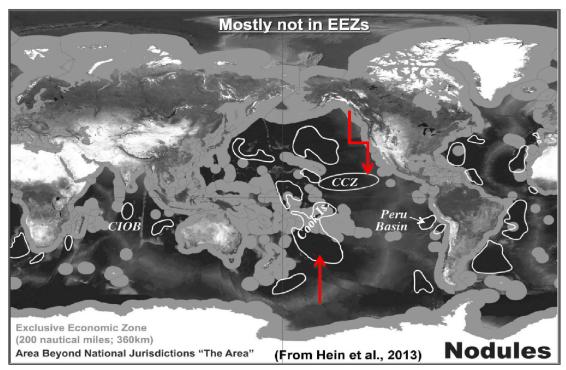


Figure 3. Global Permissive Areas for Manganese Nodules and crusts enriched in REE (From Hein et.al.2013) ⁸

Potential Polymetallic Nodule Ore Deposits

Research and exploration work so far, by private mining companies or national research organizations proved that the main potential of polymetallic nodule and Co rich crusts for obtaining REE"s as byproducts of base metals such as Mn, Ni, Co, Cu is mainly concentrated in two areas, specifically the CCZ zone and Cook Islands (see Figure 3).

- ✓ CCZ: Nickel, Copper, Molybdenum, Manganese, Cobalt, <u>REEs</u>
- ✓ Cook Is.: Titanium, Manganese, Scandium, Cobalt, REEs

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) (Hein 2012).^{7,8} (Table 2). 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 (Table 2).^{8,12}

Table 2.Comparison of land-based carbonatite ores and marine ferromanganese deposits ^{8,12}

	Grade	Tonnage	Contained Metal
	(wt.%)	(metric tons)	(tons TREO)
Bayan Obo	6%	8 x 10 ⁸	4.9 x 10 ⁷
Mountain Pass	5%	0.9 x 10 ⁸	0.45 x 10 ⁷
PCZ	0.3%	75 x 10 ⁸	2.3 x 10 ⁷
CCZ	0.1%	211 x 10 ⁸	2.1 x 10 ⁷

CCZ: Clarion-Clipperton nodule zone

PCZ: Pacific Crust Zone

The majority of economically interesting Fe–Mn nodules is concentrated in this zone of the Pacific Ocean at depths of about 5000 m at the interface between bottom waters and sediment, as well as in the upper parts of the sediment column (Koschinsky et al., 2010) ⁹(Figure 4). The CCZ contains significant numbers of areas with exploration licenses preparing future nodule mining under the auspices of the International Seabed Authority (I.S.A). The most important exploration licence was granted during 2011, to the wholly owned subsidiary of Nautilus Minerals, Tonga Offshore Mining Ltd (TOML). The Nautilus Minerals is a Canadian mining company, which early next year, will start the exploitation of the famous Solwara Cu-Au sulphide deposit in the EEZ of the Papua New Guinea State. (Figure 4).

The case of the Polymetallic nodules from the Clarion Clipperton Zone (CCZ) of the northeast Pacific Ocean

According to unofficial reports from the Tonga Offshore Mining Ltd., (personal communication D.White 2013) (courtesy by NAUTILUS Minerals) polymetallic nodules from the Clarion Clipperton Zone (CCZ) of the northeast Pacific Ocean contain total rare earth element concentrations of 800 g/t (0.08%) on a dry basis, or 600 g/t on an as received or wet basis. This translates to a Rare Earth Oxide (REO) grade of around 950 g/t or 0.095% on a dry basis.

The relative split of rare earths is: 73% lights (Ce, La, Nd, Pr), 7% medium (Sm, Eu, Gd) and 10% heavies (Tb, Dy, Ho, Er, Tm, Yb, Lu) and 8% Yttrium (Y).

Based on the average 2013 metal prices the estimated value of the contained rare earths is about US\$ 50 per wet tonne of nodules, out of a total contained metal value of US\$ 200 to 600 per wet tonne of nodules, (depending how many other metals are considered to have value and their assumed metal prices).

Potential for recovery of rare earths would have to be assessed using hydrometallurgical testwork, as there are no relevant analogies to terrestrial deposits.

Rare Earths in CCZ Polymetallic Nodules

Total rare earth element (REE) concentrations in CCZ nodules are modest, at 800 g/t (0.08%) on a dry basis, or 600 g/t on an as received or wet basis. A breakdown is shown in the following Table 3. REE are often reported and measured as oxides (REO), which have a 1.2 mass factor relative to the elements. For the composition shown in this Table, of 788 g/t of REEs, the corresponding REOs are 945 g/t.

Based on March 2013 prices, as shown in Table 3, the contained value of rare earths in nodules is around US\$ 65 / dry t this equates to US\$51 / wet t assuming 20% free moisture. The breakdown of this is shown in this Table. Components of less than 10 g/t are not included in the calculation.

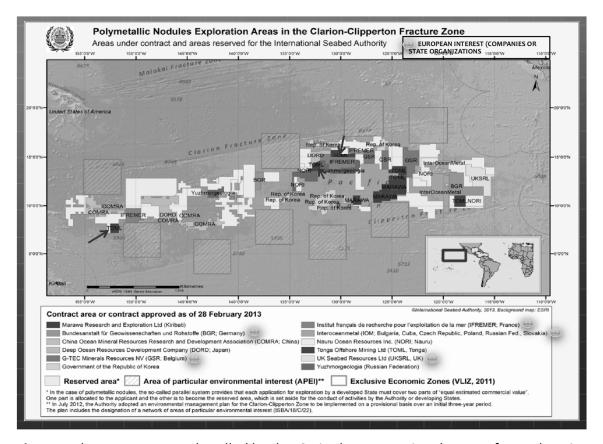


Figure 4. The contract areas handled by the ISA in the International waters for Exploration and Exploitation in State research organisations and private mining companies. The areas of special interest with nodules and crusts rich in REE are shown with arrows, whilst with a special symbol the areas handled by the ISA to companies or organisations of European interest are shown too.

Table 3. Median Rare Earth Content of CCZ Manganese Nodules¹⁰

Element	Symbol	REE, g/t	REO, g/t	Relative REO Split, %	Contained Value, US\$/ dry t of Nodules
Lanthanum	La	97	113	12	1.20
Cerium	Ce	316	388	41	4.31
Praseodymium	Pr	31	36	4	3.17
Neodymium	Nd	131	153	16	11.72
LRE	-	575	690	73	20.40
Samarium	Sm	34	40	4	0.94
Europium	Eu	8	9	1	-
Gadolinium	Gd	30	34	4	1.69
MRE	-	72	83	9	2.63
Terbium	Tb	5	6	0.6	_
Dysprosium	Dy	26	30	3.2	19.57
Holmium	Но	5	5	0.6	_
Erbium	Er	13	15	1.5	9.53
Thulium	Tm	2	2	0.2	_
Ytterbium	Yb	13	14	1.5	9.41
Lutetium	Lu	2	2	0.2	_
Yttrium	Υ	76	97	10	3.63
HRE + Y	-	141	171	18	42.13
Total	-	788	945	100	65.17

Comparison to Rare Earth Primary Ore Bodies

Concentrate Grades

The ore grades of a number of western world rare earth deposits are shown in Figure 5 below. Of those shown, only the Mountain Pass and Lynas Mt Weld CLD projects are operating. Based on the REO grade of CCZ nodules of 0.095%, terrestrial projects have grades of 10 to 100 times this.

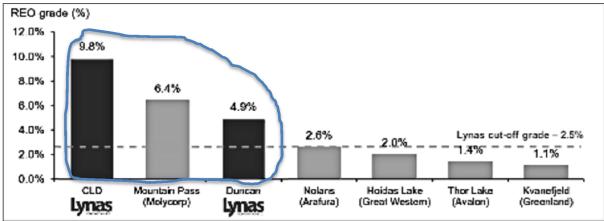


Figure 5. Total Rare Earth Grades of Some Western World Terrestrial Deposits. (LYNAS REE Special report 2014) ¹¹

Table 4. In place metal tonnages (X10⁶ metric tons)

		-	
	Clarion-	Global Land-Based	Pacific Prime
	Clipperton	Reserves ^a	Crust Zone
	Zone Nodules		
Manganese	5,929	5,200 <i>(630)</i>	1,718
Copper	224	1,000+ <i>(630)</i>	7.4
REO	17	150 <i>(110)</i>	20
Nickel	278	150 <i>(</i> 76 <i>)</i>	32
Molybdenum	12	19 <i>(9.8)</i>	3.5
Lithium	2.7	14 <i>(13)</i>	0.02
Cobalt	42	13 <i>(7.3)</i>	50
Tungsten	1.3	6.3 <i>(2.9)</i>	0.67
Niobium	0.4	3.0 (2.9)	0.4
Bismuth		0.68 <i>(0.32)</i>	0.32
Yttrium	1.9	0.48 <i>(0.42)</i>	1.7
Tellurium	0.07	0.05 (0.022)	0.45

^a USGS reserve base and 2011 reserves (reserve base includes those resources that are currently economic (reserves), marginally economic and subeconomic. Nodules tonnaged used is 21,000 million dry tons and crust tonnage used is 7,533 million dry tons (FromHein et.al.2013) ⁸

However things are not so simple if we will take into account the issue of the so-called **Rare Earth Oxide Basket Pricing.**

Rare earth projects often use a "basket price" to put a value on the products they intend to produce. This ideally is the weighted average of the price of the individual elemental components of the intended production basket. Depending on the status of a project, this information may not be available, so the same technique would be applied to either the ore or an intermediate, the composition of which can be determined.

It should be emphasized that the basket price is a nominal product value, in US\$/kg REOs of product, not the contained value of rare earths in the ore (which would be in US\$/t).

As shown in the Figure 6 below, the basket price has been quite volatile over the last 3 years, with the China FOB or international price peaking at over US\$200 /kg in 2011, when supply was restricted. Prices have now decreased significantly to less than US\$ 40 /kg. Based on the rare earth distribution in CCZ nodules, which are relatively high in the more valuable Nd, Pr and heavy rare earth components (e.g. Dy), the current basket price of contained rare earths is US\$ 65 /kg of REOs. It is evident that, this is significantly higher than that shown for the Lynas Mt Weld project, in the Figure 5 , which is approximately US\$35/kg. Finally the "basket value" of any rare earths that can be recovered is likely to be higher than those of terrestrial deposits, due to the relatively high portions of Neodymium, Praseodymium and heavy rare

earths (especially Dysprosium) (Figure 7). 8,12

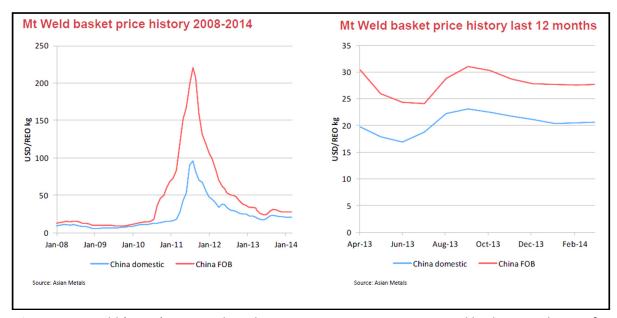


Figure 6 Mt Weld (Lynas) Rare Earth Basket Price History 2008-Jan.2014 and basket price history for the last 12 months ¹¹

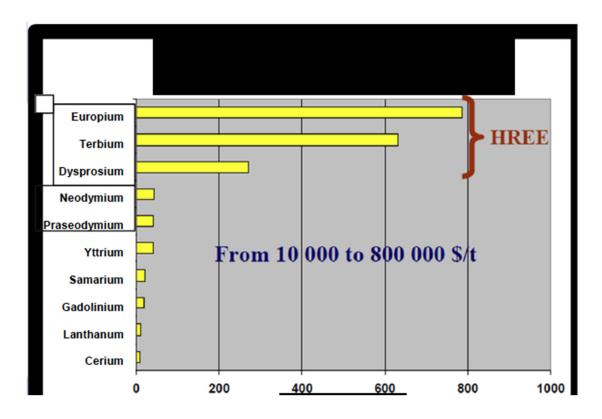


Figure 7. Light versus Heavy REE in relation to REE prices: Bayan Obo & Mountain Pass average <1% HREE-PCZ(Pacific Crust Zone) averages 6.3% HREE and CCZ(Clarion-Clipperton nodule Zone) averages 10% HREE (Hein 2011, Hocquard 2010) 12,13

Moreover for manganese nodules and Co rich crusts, rare earths should be considered as part of the byproduct that remains after extraction of the primary economic target metals, as opposed to being the primary economic target itself as in the cases of the most land based deposits i.e Mountain Pass Kutessay II,Lynas etc.. Initial extraction of the main economic target metals from the nodules and crusts (nickel, copper, cobalt and manganese) can significantly enhance the rare earth concentrations for subsequent extraction. In the metallurgical processing methods considered to date, the material that would be processed for REEs would be what is left behind after the target metals are removed. Thus this processed product is what should be used to compare with other sources of REEs.

Primary Ore Versus Byproduct Production and environmental considerations

Based in the above comments it is very important to make some simple comparisons between the land-based REE primary ore deposits and the REE or REO (Rare Earth oxides) which can be produced as byproducts from manganese nodules and cobalt rich crusts. Thus:

Tand-based: REE predominantly primary ore

PCZ: Byproduct of Co and Ni mining

CCZ: Byproduct of Ni and Cu mining

Moreover the attractiveness of nodules as a rare earth source is enhanced by their low uranium-thorium content. The mean values of uranium and thorium of the manganese nodule samples in this study are 3.6 ppm and 22 ppm respectively. This level of uranium would not be considered either a potential contaminant or a byproduct, as "It occurs naturally in low concentrations of a few parts per million in soil, rock and water" (Wikipedia, 2011). The thorium value is substantially lower than many existing terrestrial rare-earth ores (which contain a few hundred ppm to thousands of ppm) ¹³.

Thorium Concentrations

Most of land based deposits i.e Bayan Obo and Mountain Pass contain 100s ppm Th

- •PCZ averages 11 ppm Th
- •CCZ averages 14 ppm Th

Assumptions and expectations from delivering REE as byproducts of the main economic metals in nodules and crusts i.e Ni,Co,Cu and Mn.

Spickermann (2012) ¹⁰ assumes the REE would remain in the residue after base metals extraction and as a consequence would be more concentrated and presumably amenable to extraction. He believes that "the manganese nodule REE relative content increases dramatically after the NI, Cu, Co and Mn are extracted". This assumption seems to be sensible. It is valid to assume that modern, targeted, efficient metallurgical processing associated with the extraction of these four minerals leaves the bulk of the rare earths in the residual material, and that it is this residual material that is processed for REEs.

One may also assume that the adsorbed and structural water content associated with the MnO_2 of the nodule is also removed. According to the same author "taken together, these

constituents measured 69.3% of the CCZ nodules as follows: 9.6% adsorbed water, 8.0% structural water, 48% MnO₂, 3.7% NiO + CuO + CoO. This gives (in the ideal case where no REE are lost in processing) a beneficiation multiplier of 3.25". However a general characteristic of REE processing is that heavy rare earth extraction and recovery is significantly lower than the medium and light fractions." It is also possible that the REE would be extracted, at least partially, along with base metals, in a pressure acid leach.

Possible recovery techniques include precipitation and solvent extraction. Spickermann pointed out that "the beneficiation due to the removal of Ni, Cu, Co and Mn (and water) increases the value of the heavy REEs in the Mn nodule byproduct material to \$380/tonne. This is a very attractive value, as it is 165% of Mountain Pass (approximately \$230) and 57% of Kutessay II (\$664)." (in 2011 prices).

It should be emphasized that in this case since REE will be produced as byproducts for nodules and crusts the costs of mining, transportation, initial ore grinding, and tailings disposal are borne by the four primary target metals. In the case of land based REE deposits the value of the rare earth products alone must cover these costs. According to the same author "Finally (in 2011 prices), at \$425/tonne the light REE content of the nodule byproduct material may also be of economic interest. The combined light and heavy REE content of the nodule byproduct is \$804/tone (\$248/tone before processing beneficiation)."

Very recently in an experimental study, published few months ago (D.Mohwinkel et.al.2014)¹⁴ confirmed that the nodules and crusts are enriched in critical or rare high-technology elements such as Li, Mo, Nb, W, the rare earth elements and yttrium (REY).

According to the same authors these metals could be extracted from nodules and crusts as a by-product to the base metal production. They showed that by leaching of ferromanganese nodules and crusts with desferrioxamine-B a key ingredient of the method they have developed, that a significant and selective extraction of high-tech metals such as Li, Mo, Zr, Hf, the REE Nd,Ce,Dy and Ta is possible, while other elements like Fe and the base metals Mn, Ni, Cu, Co and Zn are not extracted to large extents.

Given that almost all elements considered to be of high importance for the high-tech industries are — almost exclusively— allocated in the iron-oxyhydroxide phases, a ligand specialized in the selective dissolution of iron oxides, such as siderophores, is a promising candidate for selectively leaching of elements such as Zr, Hf, Nb, Ta, the rare earths and W. These authors claimed that they were able to extract up to 80% of four rare earth metals from ferromanganese nodules by refining their ore-leaching method.

These new findings confirm Spickermann's ¹⁰ suggestions, creating a very promising prespective in the near future, provided that future metallurgical testwork programme on nodule and crusts processing for recovery of rare earth will be undertaken.

Concluded remarks

1.It is now well established the importance of some shallow and deep sea mineral formations as a new source for REE. The shallow marine water exploration and mining for placer deposits (light heavy minerals) is already an important ongoing activity in the Continental shelf of

Easter Africa and Sri Lanka, South East Asia, Australia. Placer deposits containing titanium, thorium, rare earth elements and zirconium have been mined at a location on the southeast coast of Sri Lanka. Numerous undeveloped placer deposits of light heavy minerals (ilmenite, rutile, magnetite, zircon, garnet, and monazite) are present on beaches and offshore in the Indian sub-continent.

2.In Greece and especially in some areas of the N.Aegean Sea Continental Shelf (on the Strymonikos plateau off eastern Macedonia) there is an extensive polymetallic heavy minerals mineralisation rich in titanium, rare earths, thorium, uranium and traces of gold in the form of sandy formation. A publication by the Greek Geological Survey (IGME) during 2002 gives as total estimated resources (coastal and underwater) 490 x 10 6 tn, with an average REE content about 1.17%.

This sandy formation rich in heavy minerals shows high content of Allanite estimated at an average value of 2.39%. This mineral is mainly responsible for the high content in REE (mainly lights), Th, U, etc.

- 3.The exponential advances on exploration, exploitation, beneficiation techniques as well as mining technology concerning deep sea mineral resources, proved that there is a distinct REE type of mineralisation associated with deep sea polymetallic nodules and cobalt rich crusts. Both types of mineralisations are primary i.e many nodule deposits show both a diagenetic and a hydrogenetic compound due to accumulation of metals both from pore water and from seawater. These nodules are characteristic for the abyssal plains e.g. within the Clarion Clipperton Zone (CCZ) in the Central Pacific. Ferromanganese crusts and nodules represent an important near future resource, since they not only contain base metals such as Mn, Ni, Co, Cu and Zn, but are also enriched in critical or rare high-technology elements such as Li, Mo, Nb, W, the rare earth elements and yttrium (REY). Both types have a significant potential to supply REEs to the marketplace as a byproduct of the extraction of copper, nickel, cobalt, and manganese.
- 4. 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.

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.

5. During the recent ongoing exploration process from the wholly owned subsidiary of Nautilus Minerals, Tonga Offshore Mining Ltd (TOML), specially targeted research for the rare

earth distribution in CCZ nodules, showed that they are relatively high in the more valuable Nd, Pr and heavy rare earth components (e.g. Dy). This means that the basket price(in 2013 average REE prices) of contained rare earths is US\$ 65 /kg of REOs. Unsurprisingly, this is significantly higher than that shown for some of the most important land based deposits such as the Lynas Mt Weld project, which is approximately US\$40/kg.

The relative quantities of the more valuable rare earth components is higher in nodules than terrestrial ores. This results in a nominal product basket price approximately 60% higher than product mixes from terrestrial deposits, though it should be emphasised that there is no knowledge of possible recovery profiles. (Data provided from personal communication and courtesy from Tonga Offshore Mining Ltd.).

- 6. For manganese nodules and Co rich crusts, rare earths should be considered as part of the byproduct that remains after extraction of the primary economic target metals (Ni, Co, Cu, Mn) as opposed to being the primary economic target itself as in the cases of the most land based deposits i.e Mountain Pass Kutessay II,Lynas etc. it is sensible to assume that initial extraction of the above main economic target metals from the nodules and crusts (nickel, copper, cobalt and manganese) can significantly enhance the rare earth concentrations for subsequent extraction. In the metallurgical processing methods considered to date, the material that would be processed for REEs would be what is left behind after the target metals are removed. Thus this processed product is what should be used to compare with other sources of REEs.
- 7. The attractiveness of nodules as a rare earth source is enhanced by their low uranium-thorium content. The mean values of uranium and thorium of the manganese nodule samples rarely exceeds the 4 ppm and 22 ppm respectively. This level of uranium would not be considered as a potential contaminant.
- 8. It is clear that extensive and in depth investigation is necessary in order to fully clarify the prospects of recovering rare earths metallurgically at industrial level, from nodules and crusts, at this stage.

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