MINDeSEA

Seabed Mineral Deposits in European Seas: Metallogeny and Geological Potential for Strategic and Critical Raw Materials

MINDeSEA

Deliverable 6.2: Report of the polymetallic nodules prospect evaluation parameters that will be employed as a road map for the creation of the polymetallic nodules occurrence database

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6.2. Report of the polymetallic nodules prospect evaluation parameters that will be employed as a road map for the creation of the polymetallic nodules occurrence database

Summary:

GeoERA is a Co-Fund ERA-NET action under Horizon 2020, towards "Establishing the European Geological Surveys Research Area to deliver a Geological Service for Europe". Its main objective is to contribute to the optimal use and management of the subsurface.

The project “Seabed Mineral Deposits in European Seas: Metallogeny and Geological Potential for Strategic and Critical Raw Materials” (MINDeSEA), materialized in the frame of the GeoERA Raw Materials Theme (Grant Agreement Nº 731166, project GeoE.171.001), resulted from the collaboration between eight GeoERA Partners and four Non-funded Organizations at various points of common interest for exploration and investigation on seafloor mineral deposits.

This document starts by giving a general overview about the Polymetallic Nodules, concerning their textural and chemical characterization, how they are formed and where do they exist.

Secondly, this document identifies the environmental parameters favouring the formation of polymetallic nodules, which are also used as a basis for defining prospective areas for seafloor exploration. The identification and compilation of these factors was gathered through published scientific results based on studies that were done in the most important and extensive nodule fields existing in the Pacific and Indian oceans. The associated permissive areas do not necessarily contain economically minable nodule deposits but simply represent regions where their formation is feasible.

Thirdly, this report briefly describes the current status of the MINDeSEA database for polymetallic nodules, namely information on the number of occurrences identified so far, as well as relevant information obtained for the previously defined metallogenetic parameters, in order to systematize and define propitious areas for the formation of polymetallic nodules. A geochemical characterization based on a restrict, but important, group of elements (Fe, Mn, Co, Ni, Cu, Rare Earth Elements - REE) is presented with the

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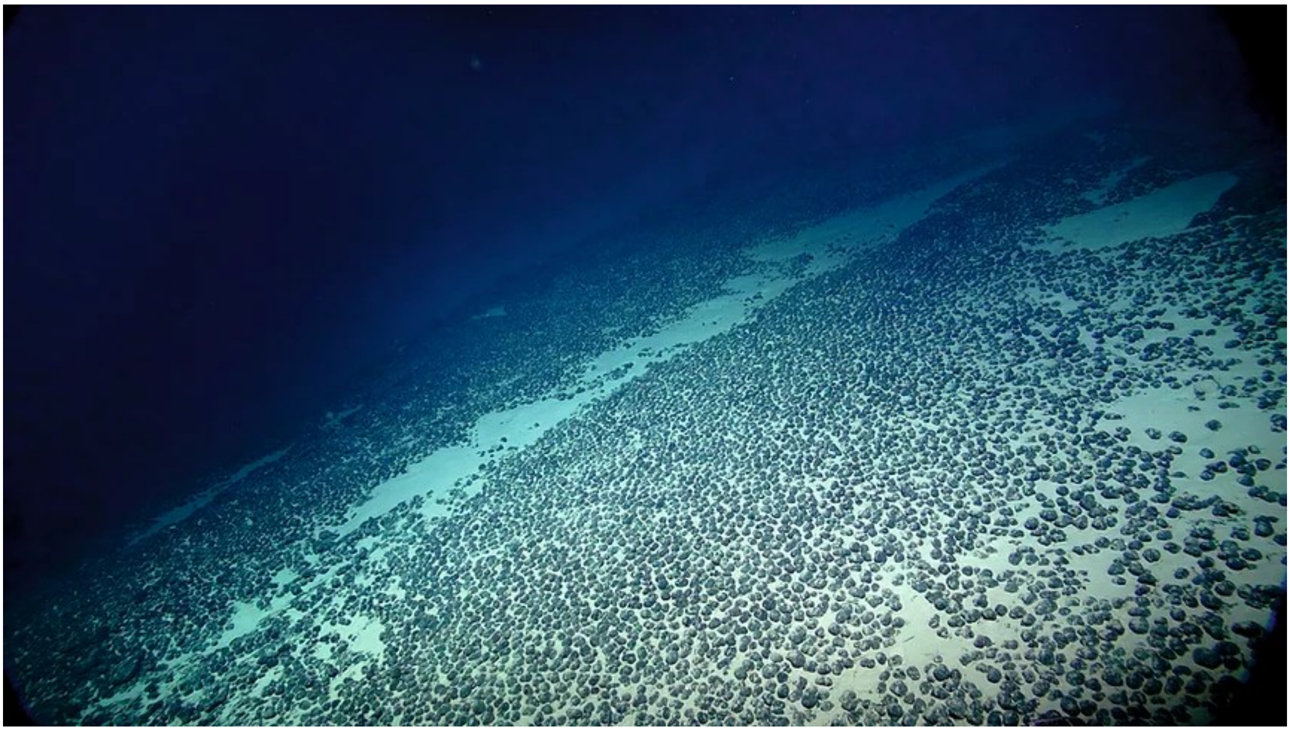
aim of identifying the formation processes associated to the registered nodules in the MINDeSEA database. All this characterization is made for each region/sub region defined by the Marine Strategy Framework Directive (MSFD) in the North-East Atlantic Ocean and Mediterranean Sea.

Finally, the report addresses the prospect evaluation parameters and the formation processes that may have controlled the generation of polymetallic nodules for each MSFD region/sub region.



Underwater image showing polymetallic nodules covering the seabed in the Tropic Seamount (Canary Islands, Central East Atlantic Ocean). Photo: ROV ISIS 6000, National Oceanographic centre, UK.

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1. Introduction

1.1. Polymetallic Nodules: what are they?

Polymetallic nodules are marine sedimentary mineral deposits, composed mostly of iron and manganese, that precipitate very slowly from seawater (hydrogenetic) or from bottom sediment pore waters (diagenetic). In Addition to these two elements, the polymetallic nodules contain numerous other elements, many of which are rare and valuable metals that can reach concentrations that are economically valuable, including some critical metals, platinum group metals, and the rare earth elements (REE) (e.g. Hein & Koschinsky, 2014).

Polymetallic nodules can have different size, shape, and surface morphologies. Concerning the size parameter, nodules generally range from about 1 to 12 cm in their longest dimension. Some extremely large specimens of 21 cm have been found in the Peru Basin (von Stackelberg, 1997, 2000). but they can also have millimetric scale dimensions (micronodules). Typically, the most common dimensions are between 1-5 cm. In terms of shape, typically include spheroidal, ellipsoidal, elongated, discoidal, platy, botryoidal or irregular forms. The surface morphologies can be smooth or coarse-grained, with the smooth side being in contact with seawater and the coarse side being surrounded by sediment (Murton *et al.*, 2000).

The nodules' internal growth structures are characterized as being finely laminated, columnar, pillar-like, dendritic, and massive. Hydrogenetic layers are typically composed of finely laminated to columnar structures, whereas diagenetic precipitation mainly leads to the development of dendritic layers and less frequently to dense, massive layers (von Stackelberg & Marchig, 1987).

Various Fe oxyhydroxide and Mn oxide are the dominant minerals that compose polymetallic nodules, and additional metals are incorporated into these main phases. The mineral composition of hydrogenetic layers consists predominantly of poorly crystalline Fe bearing vernadite (also called δ -MnO_2), and X-ray amorphous iron oxyhydroxide (Hein *et al.*, 2000). Diagenetic layers mainly consist of turbostratic phyllomanganates,

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such as 10 Å vernadite and, to a minor amount, of 7 Å vernadite, birnessite, asbolane, romanechite and todorokite (Wegorzewski & Kuhn, 2015; González et al., 2016). Cations sorb onto the Mn oxide, which has a strong negative surface charge at seawater pH. In contrast, the negative and neutral element complexes dissolved in seawater sorb onto the slightly positively charged surface of Fe oxyhydroxide (Koschinsky & Hein, 2003).

1.2. Polymetallic Nodules: how do they form?

Polymetallic nodules grow by mineral precipitation in concentric banded zones of micro-layers around a minute nucleus (Figure 1), that is commonly composed of a fragment of an older nodule, rock fragment, or even by biogenetic fragments (von Stackelberg & Beiersdorf, 1991). Individual layers are characterized by different textural, appearance as well as chemical and mineralogical compositions, which are determined by their origin processes (Hein & Koschinsky, 2014). There are two principal processes leading to the

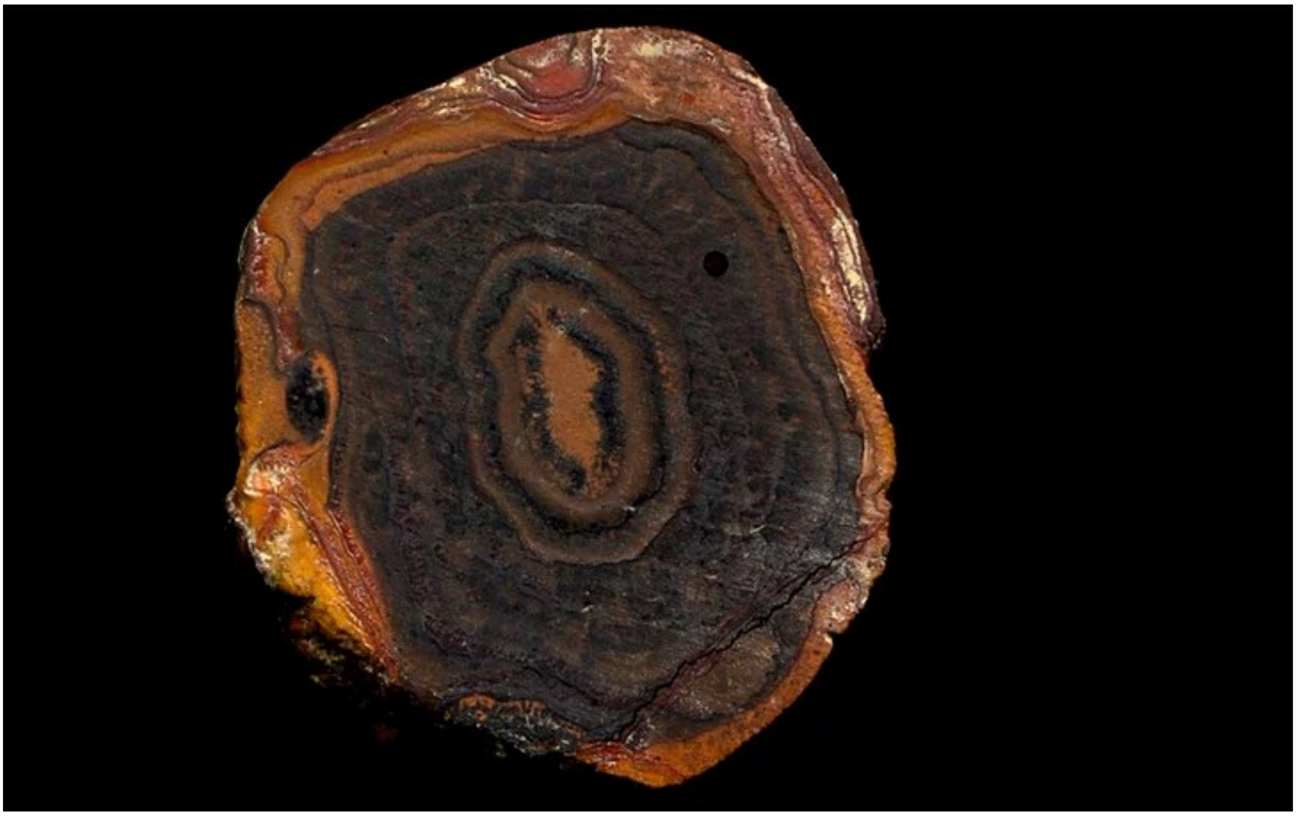

Figure 1. Photograph showing the internal concentric structure of a spherical small polymetallic nodule section, 2 cm wide (Guadalquivir Diapiric Ridge área, Gulf of Cádiz, North-East Atlantic Ocean). Source: González *et al*., 2009 (https://doi.org/10.1016/j.margeo.2008.11.005).

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formation of ferromanganese oxides under marine conditions: hydrogenetic precipitation and diagenetic precipitation. In the first mechanism, the hydrogenetic layers, that build the nodules structure, are formed by metal precipitation from oxic near-bottom seawater and/or oxic sediment pore-water, whereas diagenetic layers are formed by metal mobilization in the suboxic pore water and precipitation at the suboxic/oxic interface. Apart from Mn and Fe oxide layers, a certain amount of deep-sea sediment also occurs in the pore space of the nodules. Hence, nodules occur that are solely hydrogenetic (as in seamounts) or solely diagenetic (as in Peru Basin), but most nodules are a combination of both (e.g. Kuhn *et al*, 2017).

The growth rate of hydrogenetic layers is typically in the range of 1–5 mm per million years, (Koschinsky & Hein, 2003), whereas diagenetic layers grow considerably faster (up to 250 mm per million years; von Stackelberg, 2000). Because most nodules form by hydrogenetic and diagenetic precipitation, they grow at intermediate rates of several tens of mm/Ma years (the greater the diagenetic input to nodules, the faster the growth rate.) and usually have an age of several millions of years (Hein & Koschinsky, 2014).

Recent studies demonstrate that metal enrichment and the structural incorporation of minor and trace metals in deep-ocean polymetallic nodules is controlled by the mineralogy of the nodule (e.g. Koschinsky *et al*, 2020). As a result, nodule formation processes — hydrogenetic versus diagenetic precipitation — that control the mineralogy of the polymetallic nodules also govern their chemical composition (e.g. Kuhn *et al*, 2017).

The elements dissolved in seawater are derived predominantly from land via rivers and wind-blown dust, which then dissolve to various degrees forming ions and complexes. Another source of elements to seawater is hydrothermal venting that occurs along the 89,000 kilometres of oceanic spreading centers and volcanic arcs, which is the source of most manganese and some iron dissolved in seawater. Hydrogenetic precipitation is driven by the oxidation of dissolved Mn^{2+} and Fe^{2+} in oxygen- rich ocean waters and subsequent accretion of Mn^{4+} and Fe^{3+} oxide colloids around a nucleus (e.g. Koschinsky, & Hein, 2003).

The metals present in the pore-fluids are derived from diagenetic oxidation-reduction (redox) reactions that occur in the sediment layers, then diffuse upward and are incorpo-

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rated into the Mn and Fe minerals forming at the seabed. Oxidation of organic matter in deep- ocean sediments results in the reduction and dissolution of Mn oxides and release of associated elements (Ni, Cu, Li, among others: Koschinsky & Hein, 2017). Owing to concentration gradients in the sediment, these metals diffuse upwards and, in contact with oxygen- rich ocean water, are reoxidized, leading to the precipitation of Mn oxides (Kuhn *et al*, 2017). The pore-fluids are the predominant source of Ni and Cu, whereas seawater is the dominant source of Co.

1.3. Chemical composition of Polymetallic nodules

The chemical composition of nodules varies at different scales: on regional, local, inter- and intra-nodule. In general, the chemical composition of nodules is controlled by the ratio of the hydrogenetic to diagenetic components and whether the diagenetic component results from oxic or suboxic diagenesis (Glasby, 2000); the location (geographic position and water depth), and the growth rate can also influence the nodules' chemistry.

Hydrogenetic nodules have Mn/Fe ratios ≤5 (Halbach *et al.,* 1989) and high contents of high field strength elements such as Ti, REE, Y, Zr, Nb, Ta, Hf as well as elements that can be oxidized on the surface of Mn oxides such as Co, Ce, and Te, low Y/Ho and high Th/U ratios (Koschinsky & Hein 2003; Hein *et al.* 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 (as an example, maximum total REEs plus Y in the Clarion Clipperton Zone - CCZ nodules are of about 0.08%). Lead, which sorbs onto Fe oxyhydroxides (Koschinsky & Hein 2003), occurs in much higher concentrations in hydrogenetic deposits because the Fe minerals are much more abundant in hydrogenetic than in diagenetic-influenced nodules.

Diagenetic nodules are characterized by much higher Mn concentrations than in hydrogenetic nodules, with Mn/Fe ratios >5 (*Halbach et al.,* 1988). Traditionally, Ni and Cu have been the metals of greatest economic interest (with concentrations reaching more than 1wt%), but this type of nodules are also significantly enriched in Ba, Zn, Mo, Li, and Ga (Lithium is especially high in diagenetic nodules, averaging 311 ppm in Peru Basin nodules (Hein & Koschinsky, 2013)). Other geochemical characteristics include: low Co and

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Ce concentrations, high Y/Ho ratios and low Th/U ratios (e.g. Wegorzewski, & Kuhn, 2014).

Globally, platinium-group elements (PGEs) are generally low in nodules (as an example, Pt concentrations in CCZ nodules are in the order of a hundred ppb) and not of economic interest.

1.4. Polymetallic Nodules: where are they?

Polymetallic nodules occur throughout the global ocean, from the flanks of seamounts to the abyssal plains of the deep ocean. They are also known from shallow seas such as the Baltic Sea and from freshwater lakes, but these nodules have considerably lower contents of valuable metals (e.g. Glasby *et al.* 1997). Predominantly, polymetallic nodules occur as potato-shaped concretions on the surface of sediment-covered abyssal plains, at water depths of approximately 3500 to 6500 m, forming two-dimensional deposits on top or within the first 10 cm of the deep-sea sediments. 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 Basin** (including the Cook Islands EEZ); a large nodule field also occurs in the **Central Indian Ocean basin** (these are the only know nodule fields of economic importance); polymetallic nodule fields may also occur in the Argentine Basin in the SW Atlantic and in the Arctic Ocean, although those areas are poorly explored (Figure 2). The CCZ is the area of greatest economic interest and is an area where 16 exploration contracts of about 75,000 km^2 each (one exception of 58,620 km^2) have been signed and another is pending to be signed with the International Seabed Authority (https://www.isa.org.jm/exploration-contracts/polymetallic-nodules). In general, fewer large abyssal plains exist in the Atlantic and Indian Oceans compared to the Pacific because their topography is dominated by mid-ocean ridge systems – however there are vast areas on the Atlantic made by abyssal plains.

The CCZ and Central Indian Ocean Basin nodules, which represent mixed hydrogenetic–diagenetic nodules, have similar compositions, with high Mn, very high Ni and Cu, and moderate Co, Mo and Li contents (e.g. Hein *et al.*, 2013); nodules from the Peru Basin, which primarily form through diagenetic processes, are characterized by high Mn and

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very high Ni and Li contents (Hein & Koschinsky, 2014) and the Penrhyn Basin nodules, which primarily form through hydrogenetic precipitation, have the highest Ti, Co, Y and total rare earth elements content of the three nodule types (Hein *et al,* 2015).

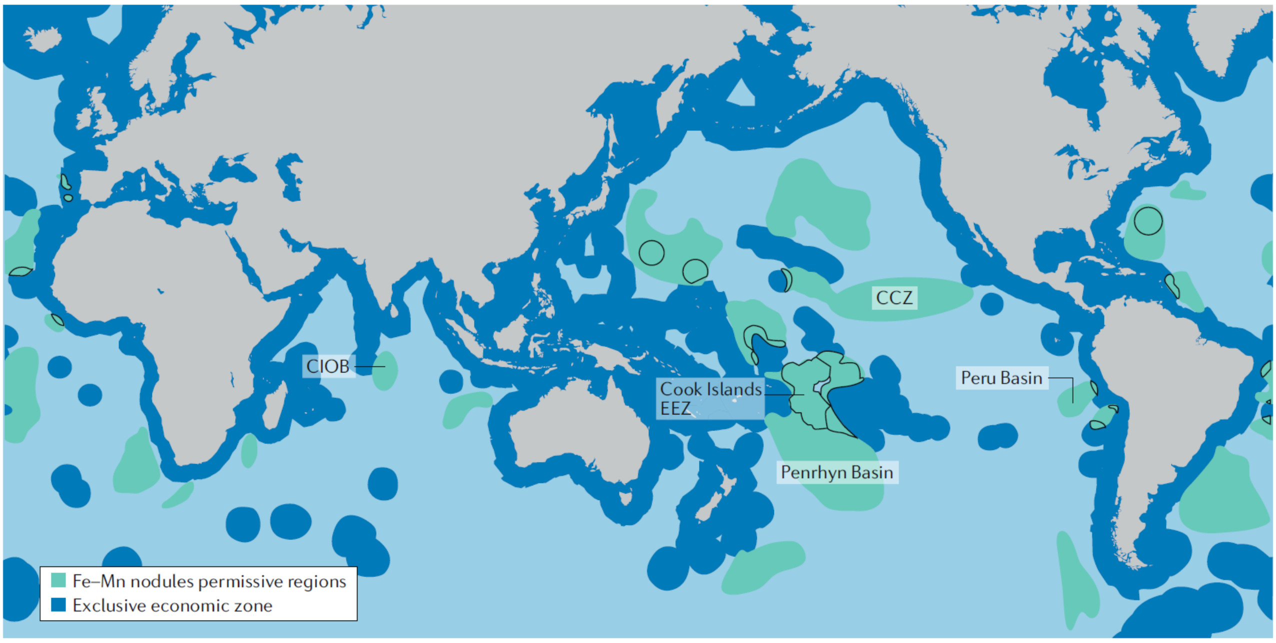

Figure 2. Global permissive areas for deep- ocean polymetallic nodule deposits. Global map showing the location of the polymetallic nodules permissive regions and the exclusive economic zones (EEZs). The four best known polymetallic nodule fields are the Clarion–Clipperton Zone (CCZ), Peru Basin, Penrhyn Basin (including the Cook Islands EEZ) and Central Indian Ocean Basin (CIOB). (Figure from Hein *et al.,* 2020)

Apart from the abovementioned four areas which have been the target of nodule exploration for several decades, there are many other locations in the world oceans where manganese nodules occur. Additional promising areas for investigation could be the abyssal plains in the Atlantic Ocean, which have been omitted from intense exploration so far. Another important but special region in terms of Mn nodule formation is the Baltic Sea, and manganese nodules and other ferromanganese precipitates of special formation have been reported from the Gulf of Cadiz and the Galicia Bank offshore Spain (González *et al.* 2012, 2014, 2016). Since these areas are included in the marine regions that are the subject of study by this project, they will be later addressed in the present report.

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1.5. Environmental parameters favouring the formation of polymetallic nodules

Nodule formation is favoured by a range of environmental factors, which are also used as a basis for defining prospective areas for seafloor exploration. The associated permissive areas do not necessarily contain economically minable nodule deposits but simply represent regions where their formation is feasible.

The most important polymetallic nodules 'fields are located in the abyssal plains of the deep ocean, in about 4000–6000 m water depth in all major oceans, meaning that **depth** is an important favouring factor for their generation. Besides the probable control of water depth in the formation of the nodules, this parameter could also control the concentrations of their constituent metals.

Another factor that could control the formation of the nodules is their **geographic location**. This factor is related with **biological primary productivity** (production of organic matter by phytoplankton that will supply organic carbon to the diverse heterotrophs organisms, particularly the zooplankton) in surface waters, which in turn controls the **calcite compensation depth** (CCD -the depth at which calcite dissolves quicker than it can accumulate) (Hein & Koschinsky, 2014)) – these two last factors are 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). Nodules are associated with low surface primary productivity (which also supply sediment-dwelling bacteria with sufficient organic matter for use in diagenetic reactions that release metals to the pore-fluids), typically found in the open ocean far removed from highly produc-tive upwelling regions, which are as-sociated with high sedimentation rates that are unfavorable for nodule formation. The highest-grade nodules form near, but generally below, the CCD (ISA, 2010).

Higher productivity is observed on the equator, along the coasts (especially eastern margins), and in the high latitude ocean. A major driver of these patterns is the upwelling and/or mixing of high nutrient subsurface water into the euphotic zone, as is evident from surface nutrient measurements (Sigman, & Hain, 2012). Interactions among the above referred factors (depth, biological productivity and the CCD) were emphasized by some authors (e.g. Halbach *et al.* 1988) when modelling the formation of the polymetallic nodules

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in the CCZ area – this area is located just north of the equatorial high bioproductivity zone. The combination of water depth and surface bioproductivity in the CCZ leads to its seafloor being near or just below the CCD. Areas further to the south (close to the equator) are subject to high bioproductivity and high sedimentation rates, leading to a deepening of the CCD. Under such conditions, widespread manganese nodule growth is hampered. The formation of siliceous ooze close to the CCD provides the necessary metal content and the physical properties (such as permeability for the mobility of metals in pore water) for the growth of large diagenetic nodules. The slow subsidence of the seafloor as well as the slow plate motion to the northwest as a consequence of seafloor spreading and oceanic crust alteration together with a constant sedimentation rate provides optimal conditions over a geological time span (a few million years) for Mn nodule growth. Over a period of several million years the CCZ has moved from being an area with optimal conditions for Mn nodule growth to an area with suboptimal conditions, leading to the growth of smaller nodules. This is mainly due to the greater water depths together with lower bioproductivity and particle flux rates, leading to decreasing fluxes of metals and organic material to the seafloor. This leads to a decrease in diagenetic overturn and thus to a smaller diagenetic input to the nodules. These are also the reasons for the lower nodule abundances in the Indian Ocean Basin compared to the CCZ.

Another very important factor that strongly influence the formation of polymetallic nodules is the **very low long-term sedimentation rates** of < 0.5-1.0 cm per 1,000 years, typically found on abyssal plains removed from regions of high surface productivity and terrigenous input, that is in **areas distant from continents** (e.g. Hein & Koschinsky, 2014). Such slow rates are associated with deep-sea pelagic clays, the bulk of which are allogenic (Fütterer, 2006; Glasby, 2006).

Bottom-water oxygen concentration is also an important factor controlling the nodules generation. Nodules are preferentially associated with **moderately high oxygen values** (between 150 and 210 mmol/m^3), which primarily occur in the northern and central Pacific and Indian Oceans, in the southern Pacific Ocean, and in the South Atlantic Ocean. Oxidizing conditions are critical for the formation of metallic oxides that comprise polymetallic nodules (e.g. Glasby, 1991). General absence of nodules in regions of very high and low dissolved oxygen concentration is linked to high rates of sedimentation in these areas,

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which are proximal to continental margins (Dutkiewicz *et al*, 2019).

Another important variable is **seafloor lithology**. The nodules show a strong preference for clay, followed by calcareous ooze in the vicinity of clay regions, with the remaining sediment types being relatively unimportant globally for nodule formation (Dutkiewicz *et al,* 2019). Calcareous ooze is the most widespread deep-sea lithology in the global ocean with typical sedimentation rates of 1–4 cm per 1000 years (Fütterer, 2006). This suggests that nodules occur in this substrate when the accumulation rates are low, close to the CCD which reduces the thickness of seafloor carbonate via dissolution, or where the mechanism that maintains the nodules at the surface is very efficient (von Stackelberg & Beiersdorf, 1991; Glasby, 2006).

Seafloor megafaunal biomass constitutes another factor controlling the generation of the polymetallic nodules, which typically occur in seafloor regions of **moderate to low biomass concentration** and **low total organic carbon content** (Dutkiewicz *et al,* 2019). Both of these variables are closely linked to surface productivity. Low surface productivity results in low flux of particulate organic carbon to the seafloor, which maintains benthic biomass adapted to low energy availability (Ramirez-Llodra *et al.*, 2010).

Despite average nodule growth rates being thousands of times slower than the average sediment accumulation rate, nodules persist at the sediment surface. There have been several proposals to describe the mechanism for keeping nodules at the seabed (e.g., Halbach *et al.* 1988). Two mechanisms for reducing the sediment cover, and maintaining the nodules at the surface, have been proposed in the formation of deep-sea nodules: **biological activity** (e.g., von Stackelberg & Beiersdorf, 1991; Glasby *et al.,* 2015) and **bottom currents** (e.g. Glasby, 2006; Glasby & 2015). Low to moderate concentrations of benthic megafaunal organisms, such as echinoderms, isopods, octopods, and molluscs in nodule regions would be sufficient to keep the nodules free of sediment through bioturbation and nodule lifting (von Stackelberg & Beiersdorf, 1991; Glasby, 2006), detritus feeding, and foraging (Vanreusel *et al.,* 2016) on and around the nodules. Because the nodules occur in areas of very low sedimentation the process of occasional sediment redistribution by organisms would facilitate continued growth of a nodule (Dutkiewicz *et al*, 2019).

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Bottom currents can remove fine sediments that could cover the polymetallic nodules and, at the same time, oxygenate the abyssal plain where they grow (Lusty & Murton, 2018). Nodules are preferentially associated with very low bottom current speeds of <5 cm/s, which pervade all major nodule fields including the CCZ. These speeds are considerably lower than speeds of >10–15 cm/s that are required to erode fine silt and clay in the deep sea (Dutkiewicz *et al*, 2019).

An alternative process, involving **seismic shaking**, has been invoked to represent a key process for maintaining the nodules on the sediment surface. (Hein *et al.,* 2020). Nevertheless, erosion and hiatuses in sedimentation are recognized as critical processes in the onset of nodule growth, whereas increased sedimentation rates and/or deposition of ash layers may, ultimately, lead to the burial of a nodule generation (Hein *et al*, 2020).

Also crucial to the nodules growing is the availability of a **source material for nucleation**, which can include minute fragments of rock debris, indurated sediment, micro-nodule fragments or even biogenetic micro-parts. Furthermore, numerous seamounts and fault zones can provide a high amount of nucleus material to initiate nodule growth (Hein & Koschinsky, 2014).

Small- scale ocean floor topography could also determine whether nodule abundances reach values that are high enough to become economically interesting (Kuhn *et al.*, 2017), and the **presence of semi-liquid sediments** that enhance the amount of pore water and diagenetic input to nodule growth can also be considered an environmental factor controlling the polymetallic nodules generation on the sea bottom.

2. MINDeSEA Project

2.1. Introduction

This MINDeSEA project (Seabed Mineral Deposits in European Seas: Metallogeny and Geological Potential for Strategic and Critical Raw Materials) aims to identify the principal types of seabed mineral resources (hydrothermal sulfides, ferromanganese crusts, phosphorites, marine placers and polymetallic nodules) in the seabed under the jurisdiction of

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European coastal States, addressing their integrative metallogenetic study and assess the potential for marine strategic minerals and Critical Raw Materials (CRM). The geographical scope of the project includes all the regional basins around Europe comprising the Atlantic and Arctic Oceans, the Mediterranean Sea, the Baltic Sea and the Black Sea.

The MINDeSEA project is compiling data and genetic models for all of these deposit types based on extensive studies carried out previously, which include geophysical surveys, sampling stations, underwater photography and ROV surveys, and mineralogical, geochemical and isotopic studies. It builds on previously and currently developed pan-European and national databases and expands strategic and CRM knowledge through compiling mineral potential and metallogenic studies of CRM resources in pan-European seas.

The objectives of the project include characterising deposit types under the jurisdiction of European coastal and their trace element content, evaluating supply potential, developing harmonised mineral maps and datasets of seabed deposits, producing mineral potential and prospectivity maps, proposing pilot zones, analysing present-day exploration and exploitation status in terms of regulation, legislation, environmental impacts and future directions and extending state-of-the-art knowledge and information on submarine minerals, metallogenic studies, standards and technologies across the European community.

One of the main motivations and importance behind the creation of this MINDeSEA is Europe’s long-term economic strategy, which is to ensure security of supply for these strategic metals as part of the Blue Growth Strategy developing sectors that have a high potential for sustainable jobs and growth as seabed mining.

The Earth’s crust provides almost all of society’s minerals and metals, the vast majority of which are currently derived from mining on land. Global metal demand is increasing, primarily linked to population growth and urbanization, and there are concerns about the security of supply of raw materials due to uneven resource distribution and geopolitics. In recent years, certain metals have been designated as ‘critical’, primarily owing to their economic importance and likelihood of supply shortage (The European Union recognized that raw materials are crucial to Europe’s economy and sustainable development and, as of 2020, identified a list of 30 CRM’s); additionally, the production of many CRM’s are restricted to just a few countries. Identifying reliable and sustainable sources of these CRM represents one of the primary factors driving the development of the deep- ocean-mining industry, especially as many CRM are at high risk of supply disruption, owing to the lack of diversity of their worldwide production. Increased diversity of CRM production and refining operations will be essential to ensure a secure supply of CRM for low carbon applications, such as green energy and green vehicles. Many of the rare metals required for these green- and high-technology applications are abundant in deep-ocean polymetallic nodules.

The main objective of WP6 is to compile, analyse and deliver the information on the existing occurrences of polymetallic nodules in the European margins, in order to assess the European resource potential and inventory on polymetallic nodules. This WP will also provide the basis for polymetallic nodules prospect identification and evaluation in European waters and identify key areas of missing information for future exploration and prospectively mapping.

2.2. Data for polymetallic nodules

It was well known that data on polymetallic nodules were scattered among national, governmental, academic and private data holders. In this way, the five funded European partners and the four non-funded partners have been collecting the dispersed polymetallic nodules data, by exploring the national databases from the various geological surveys in Europe. Another valuable and essential source used for data compilation were the data published in the various scientific journals that were searched through various databases. The map provided by the Marine Strategy Framework Directive (MSFD) in the North-east Atlantic Ocean and Mediterranean Sea, which was further divided into sub regions, was used by partners to establish the delimitations of their compilation work.

In a way to generate a harmonised dataset from the compiled data of polymetallic nodule occurrences, in a way to deliver the known extent and metallogeny of polymetallic nodules within European seas, it was previously produced a Task Guide (Deliverable 6.1 – Task Guide for MINDeSEA WP6 - Polymetallic Nodules) in which we have defined a scheme of data collection, having five main data fields: 1) General Data; 2) Metallogeny;

3) Economic Data; 4) Environment; 5) Other Data (Figure 3).

For the present report, special emphasis was given to the two first data fields – General Data and Metallogeny – which allows to characterize each polymetallic nodules occurrence, by compiling relevant data of the nodules generation controlling parameters, such as: location, geological setting, bathymetry, backscatter, sediment thickness, as well as the extend and depth of occurrence of Mn nodules. Morphology, textural characteristics, mineralogy and chemical composition and age data of the polymetallic nodules. Also compiled, when available, data from the surrounding sediments (type, composition, age, sedimentation rate, etc.). Additionally, the metallogenetic information was complement with the available geochemical data found for the nodules occurrences.

2.3. Polymetallic nodules occurrences – general characterization

Presently the MINDeSEA database has listed a total of **296 polymetallic nodules occurrences**. The majority is located in the Baltic Sea (184 occurrences, corresponding to 62% of the total) followed by North East Atlantic Ocean (in which was included some data points that are geographically inside the Arctic Ocean), having 68 nodules identified occurrences (23% of the total). The remaining occurrences (15%) are distributed through other five marine regions/sub regions (Figure 4). The location of the polymetallic occurrences is shown in various maps produced (Figures 5-10).

2.3.1. Macaronesia

In Macaronesia region the MINDeSEA database has listed four occurrences of polymetallic nodules and their positions are plotted in Figures 5 and 6. Two points are inside the Portuguese Extended Continental Shelf (ECS) and the other two, one is in the Spanish ECS and the other in its EEZ. Two distinct types of settings are identified: a typical marine setting, the deepest (~5000 m), located in the Madeira Abyssal Plain; and a seamount setting, corresponding to the other three occurrences. The only information available for the abyssal plain occurrence concerns the host rock which is an acid lava substratum (trachyte and phonolite) having Miocene age. The occurrences in the seamounts are

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	Data	FIELDNAME	Format	Information
General Data	**OBJECTID**	FID	Number	Feature ID. An internally generated identification number for each feature. Automatically generated within shape file.
	Shape	SHAPE	Geometry	Polygon
	Latitude	LAT		Degrees N/ Degrees S
	Longitude	LON		Degrees W/ Degrees E
	Country Code	CODE	Text (2)	Two letter country code, which corresponds to ISO3166- code http://www.iso.org/iso/english_country_names_and_code_elements e.g. FR, IE
	Administration	ADM	Text (40)	Legal status following the division of the Law of the Sea Convention: Territorial Sea (TS), Exclusive Economic Zone (EEZ), Extended Continental shelf (ECS) or the Area (A)
	Geographical Area	GEO_AREA	Text (40)	Atlantic Ocean, Mediterranean Sea, etc
	Sector	SECTOR	Text (40)	Canary Island Seamount Province, Eolian Islands, Gulf of Bothnia, etc
	Ocurrence/Deposit name	OCURRENCE	Text (40)	Name of occurrence/ deposit
	Mineral Ocurrence Type	OCURR_TY	Text (40)	INSPIRE CODES: occurrence, prospect, deposit, district, field
	Year of Discovery	YEAR_DIS	Number	2001, 2016, etc
	Year of Database Entry	YEAR	Number	2018, 2019, etc
	Date of Database Update	UPDATE	Date	dd/mm/yyyy (Date of last update of attributes)
Metallogeny	**Deposit Group**	DEPOSIT_G	Text (100)	Sediment-related deposits, hydrothermal deposits, volcanogenic deposits, magmatic deposits, metamorphism-related deposits (INSPIRE CODES)
	Deposit Type	DEPOSIT_TY	Text (40)	**Polymetallic nodules** -this exact wording must be entered in bold type (INSPIRE CODE)
	Setting	SETTING	Text (250)	Description of geological setting
	Geomorphic Features	GEOMORPH	Text (250)	Geomorphology of area of FeMn crust occurrence
	Age	AGE	Text (250)	Age of the mineral deposit and host rock
	Host Rock	HOST_ROCK	Text (250)	Substrate rock or sediment surrounding the ore deposit
	Metallic Commodity	METAL_COMM	Text (40)	Including precious and non-precious metals (USE INSPIRE COMMODITY CODES)
	Other Metals	OTHER_ME	Text (40)	USE INSPIRE COMMODITY CODES
	Commodity Group	COMM_G	Text (40)	Base metals, precious metals, energy metals, technological metals (USE INSPIRE COMMODITY CODES)
	Ore Minerals	ORE_MIN	Text (250)	Principal minerals/commodities (see INSPIRE)
	Gangue Minerals	GANGUE	Text (250)	Non-economic minerals (see INSPIRE)
	Ore mineral distribution	ORE_MIN_DISTR	Text (250)	brecciated, banded, micro-layered, etc
	Alteration	ALTER	Text (250)	Alteration minerals formed during/after the process of mineralization
	Morphology	MORPH	Text (250)	Shape and internal structure (thickness) of the mineral deposit
	Texture	TEXT	Text (250)	Banded, columnar, mottled, etc
	Geochemistry	GEOCHEM	Text (100)	Link to Geochemistry table
Economic Data	**Mineral Ocurrence Type**	OCURR_TY	Text (40)	INSPIRE CODES: occurrence, prospect, deposit, district, field
	Abundance (Kg/m2)	ABUND	Number	Abundance of the polymetallic nodules expressed as kg/m2
	Deposit Size	SIZE	Text (40)	Magnitude of the mineral deposit calculated according to ProMine (unknowed, occurrence, small, medium, large, very large)
	Grade	GRADE	Text (250)	Specify assessments of grade (Mean content of manganese (Mn); iron (Fe); cobalt (Co); nickel (Ni); copper (Cu) wt%) or resource potential, if applicable
	Resources	RESOURCE	Number	Resources in Mt
	Reserves	RESERVE	Number	Reserves in Mt
	Mined Tonnage	MIN_T	Number	in Mt
	Total Tonnage	TOTAL_T	Number	in Mt
	Remaining Tonnage	REM_T	Number	in Mt
	Resource Reporting Standard/ compliancy	RES_REP	Text (40)	PERC, JORC, NI43-101, etc
	Reference for Tonnage Assesment	REF_T	Text (40)	Company ordering the assesment
	Data Scale	SCALE	Text (100)	Specify the scale in which the deposit has been mapped and delivered
	Status	STATUS	Text (250)	e.g. under exploration, research, identified deposits, hypothetical deposits, etc. (USE INSPIRE CODES)
	Operator	OPERATOR	Text (250)	Research, exploration or operating agency/company
	Exploration Type	EXPLOR_TY	Text (250)	Exploration techniques employed to describe the mineral deposit http://inspire.ec.europa.eu/codelist/ExplorationActivityTypeValue
	Cruises	CRUISES	Text (250)	Cruises identification
	Sampling Methods	SAMPLING_M	Text (250)	Type of method to recover samples (dredge, ROV...)
	Sites Number	SITES_NO	Text (250)	Sampling sites identification
	Data Provider	DATA_PROVI	Text (150)	Name of organisation providing data
	Data Provider Contact	DATA_CONT	Text (150)	The data providing **organisation/institute** contact details – email is required
	Deposit Extent	DEPOSIT_KM2	No. Double (11,4)	Area of deposit **(Sq. Km)**
	Depth to Deposit (m)	DEPTH_TO_D	No. Double (11,4)	Depth to deposit from sea surface
Environment	**Fauna**	FAUNA	Text (100)	Type of fauna (e.g. corals,...)
Other Data	**Description**	DESCRIPTION	Text (500)	Deposit summary and metallogenetic model
	Gallery	GALLERY	Image	Images on the mineralization (geophysical, sampling, textural features, paragenesis, etc)
	References	REFERENCES	Text (250)	Link to bibliographic references (DOI and/or Author, Year & Title if you wish)
	Comments	COMMENTS	Text (250)	Any additional comments or observations

Figure 3. Data collection scheme defined for the polymetallic nodules occurrences in "Deliverable 6.1 – Task Guide for MINDeSEA WP6 - Polymetallic Nodules "

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positioned at distinct depths with the following characteristics:1) Tropic Seamount, in the south of Canary archipelago, ~1700 m depth, sand and mud covering a trachytic substratum, having a Cretaceous age; 2) Atlantis seamount, in the Canary Basin, 2370 m depth, sand and mud above a basaltic bed rock, Cenozoic age. No data is reported for Antialtair seamount.

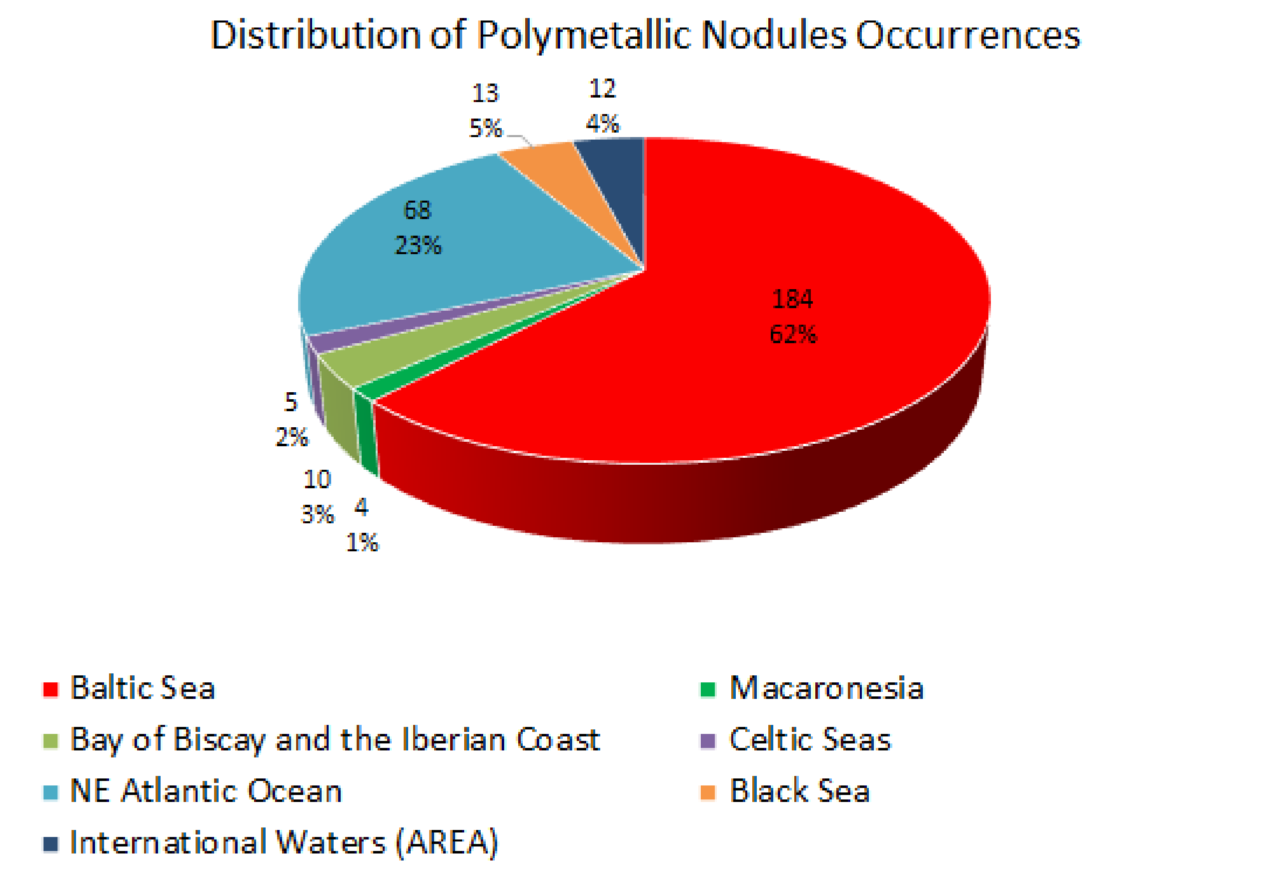

Figure 4. Distribution of the total Polymetallic Nodules occurrences (n=296) among the various MSFD regions/sub regions and International Waters.

2.3.2. Bay of Biscay and the Iberian Coast

A total of ten occurrences are reported in this region. All of them are located inside EEZ's (two in Portugal, six in Spain and one in France). A first group of five occurrences (very close from each other) is located in the Galicia Bank (corresponding to a distal domain of the western Galicia continental margin); a subgroup of three are located at depths be-

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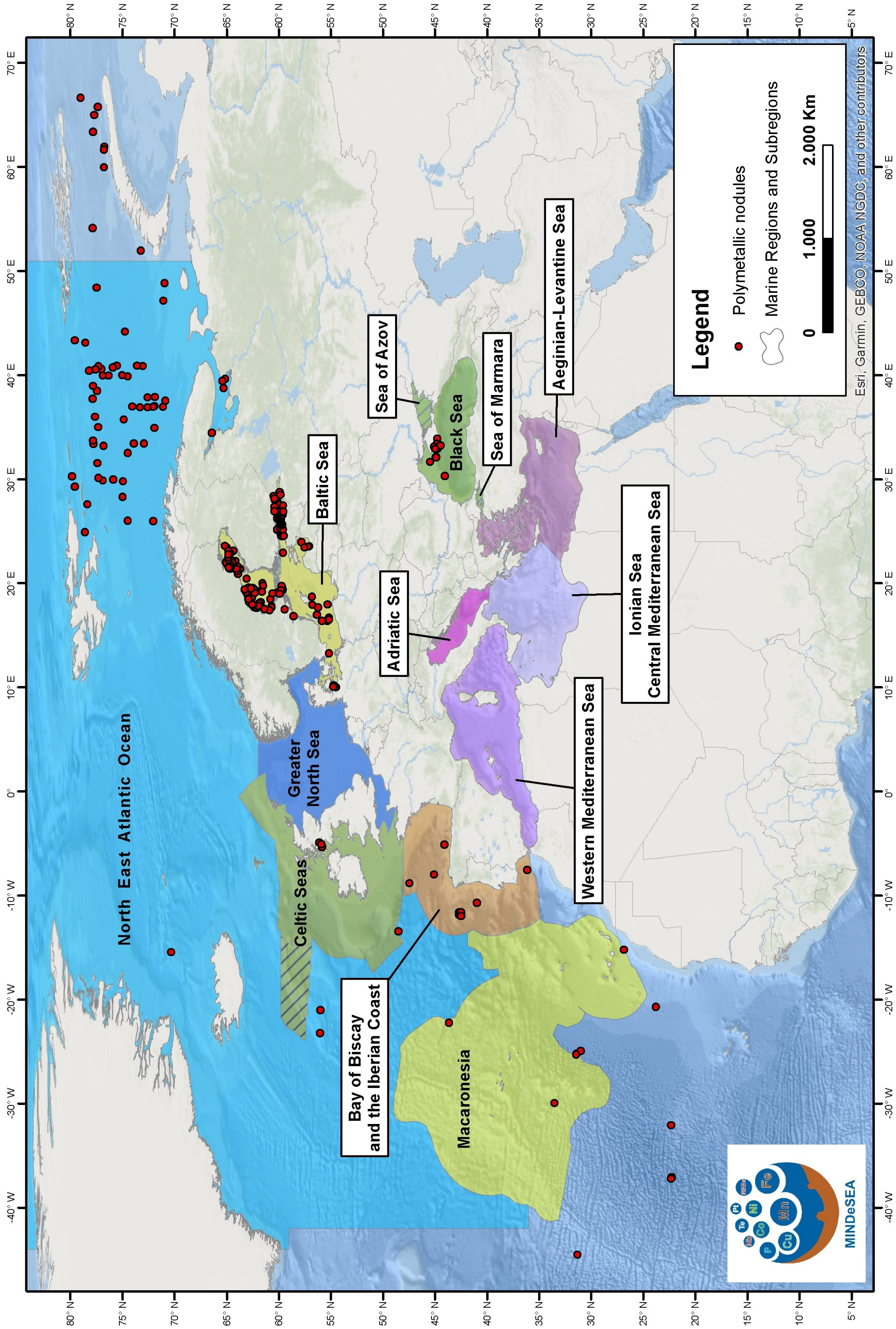

Figure 5. Spacial distribution of polymetallic nodules occurrences, in relation to the MSFD marine regions/sub regions, compiled inside the MINDeSEA project.

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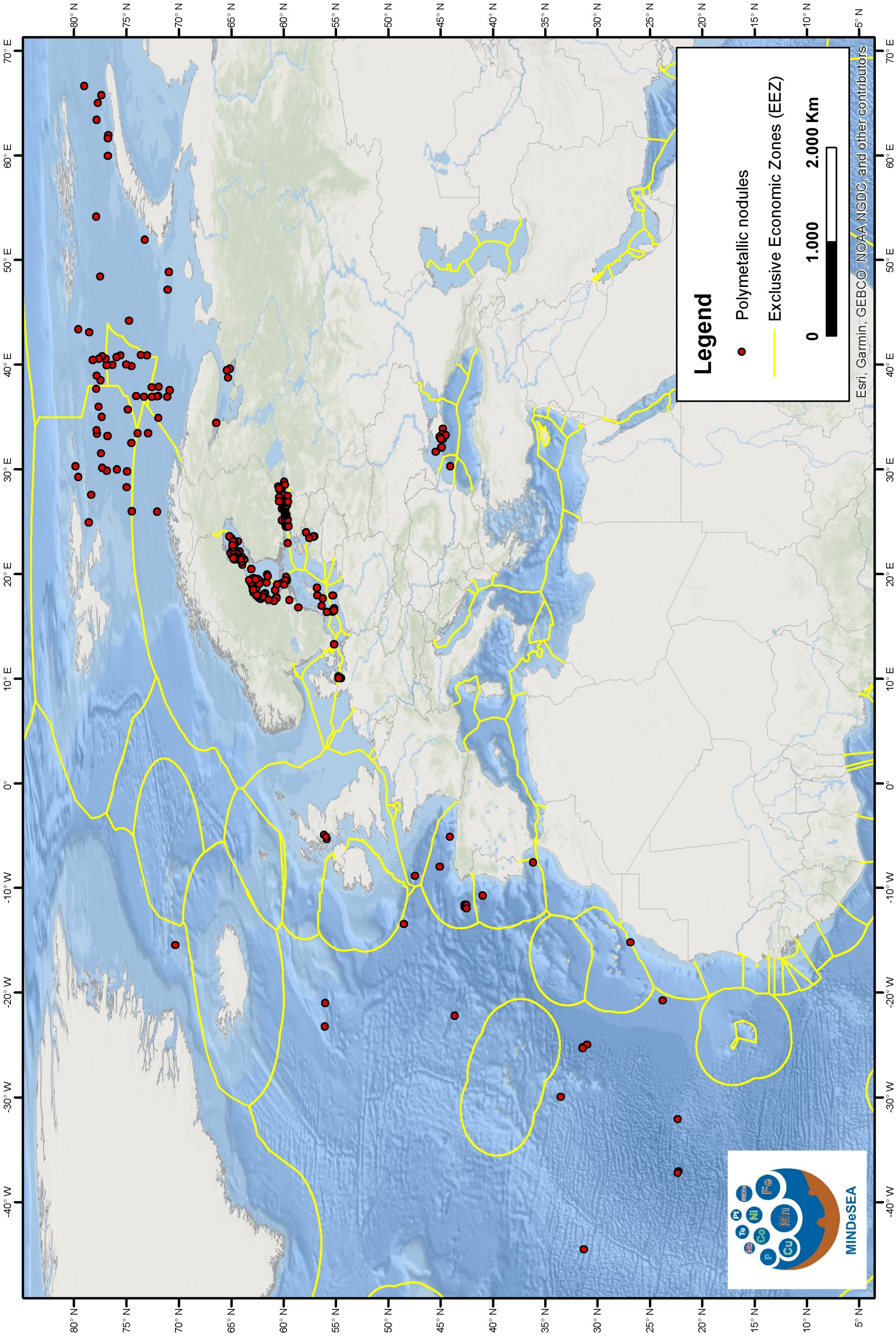

Figure 6. Spacial distribution of polymetallic nodules occurrences, in relation to the EEZ's, compiled inside the MINDeSEA

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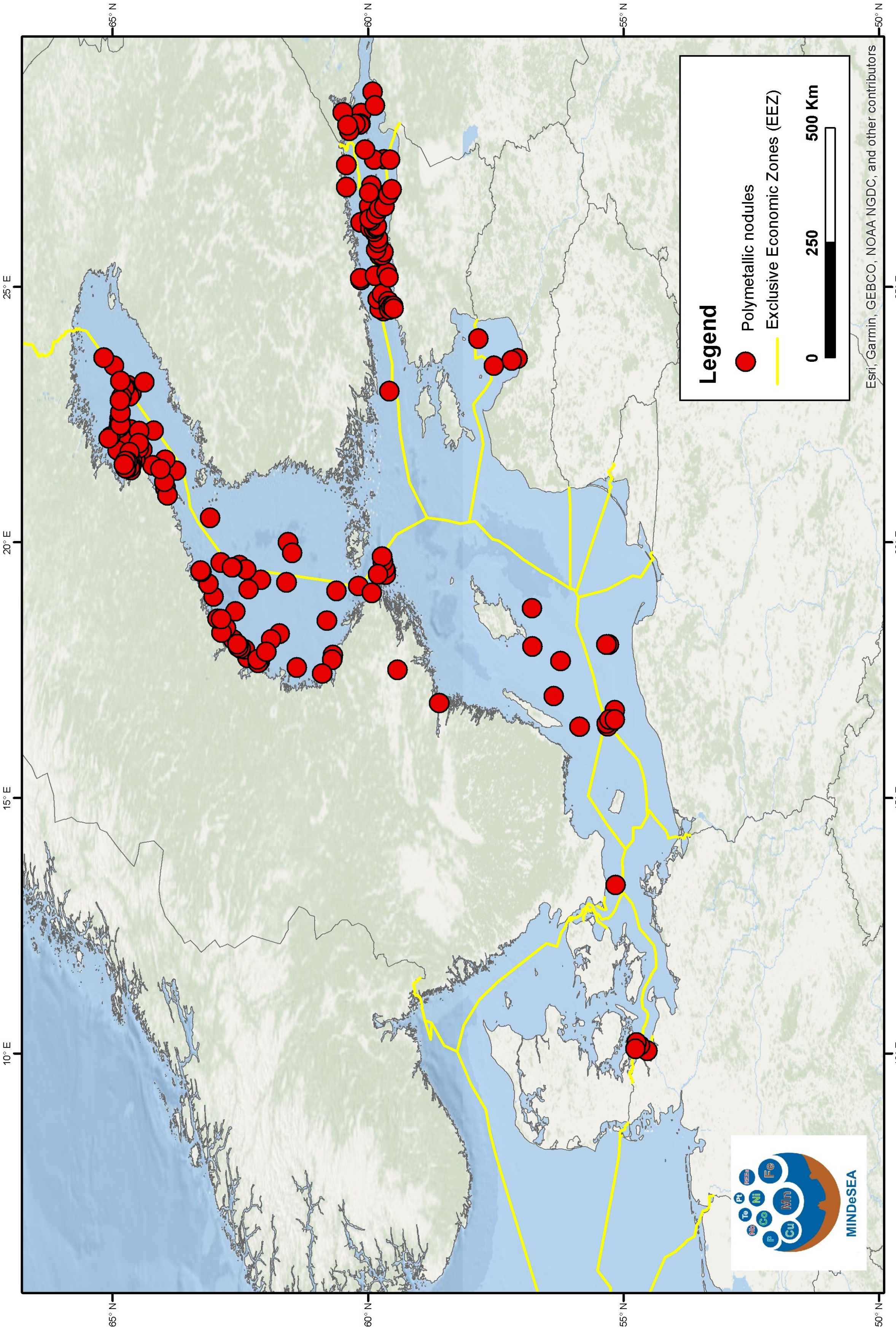

Figure 7. Spacial distribution of polymetallic nodules occurrences in the Baltic Sea (in relation to the EEZ's), compiled inside the MINDeSEA

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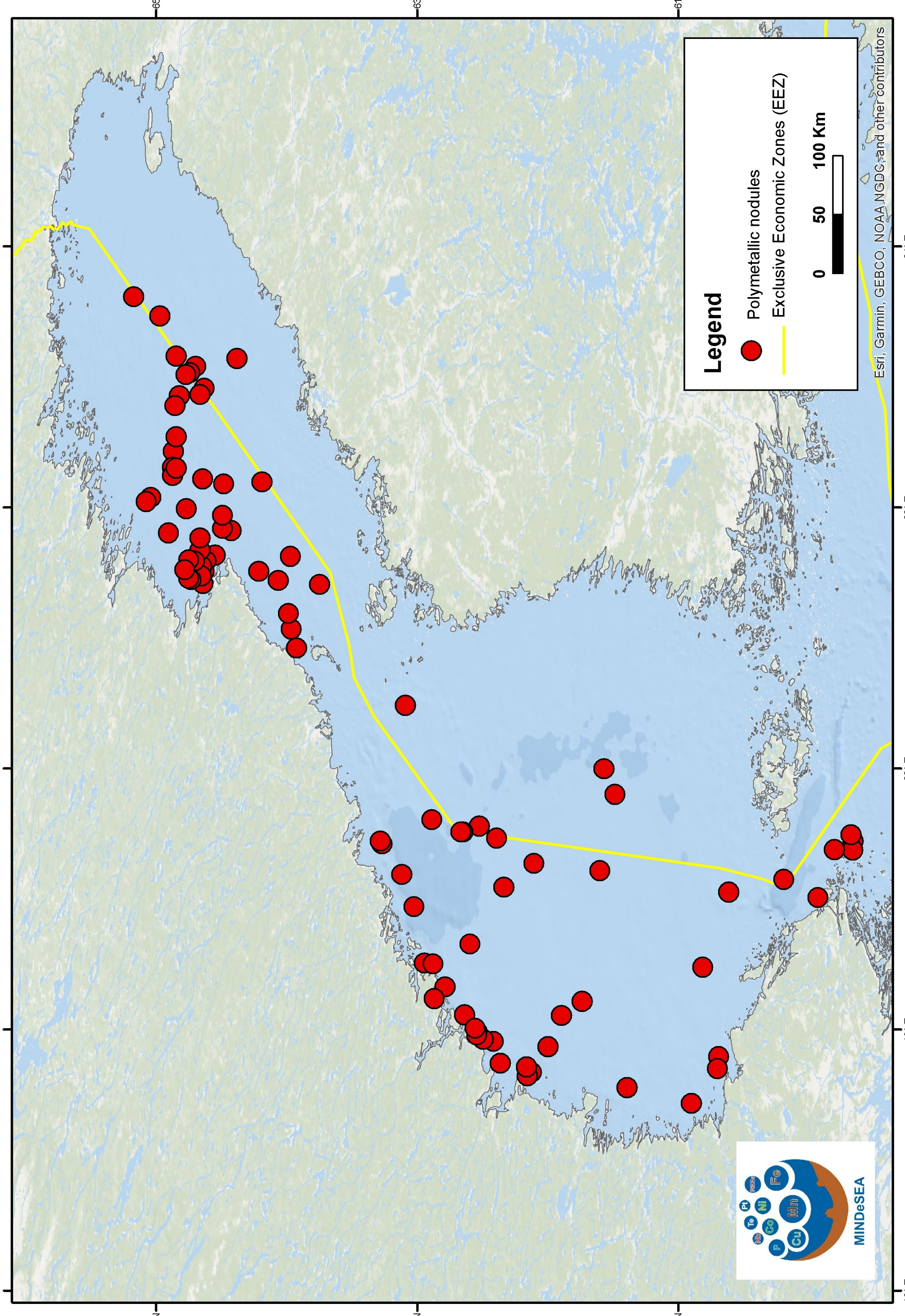

Figure 8. Spacial distribution of polymetallic nodules occurrences in the Gulf of Bothnia and Bothnian Sea , compiled inside the MINDeSEA

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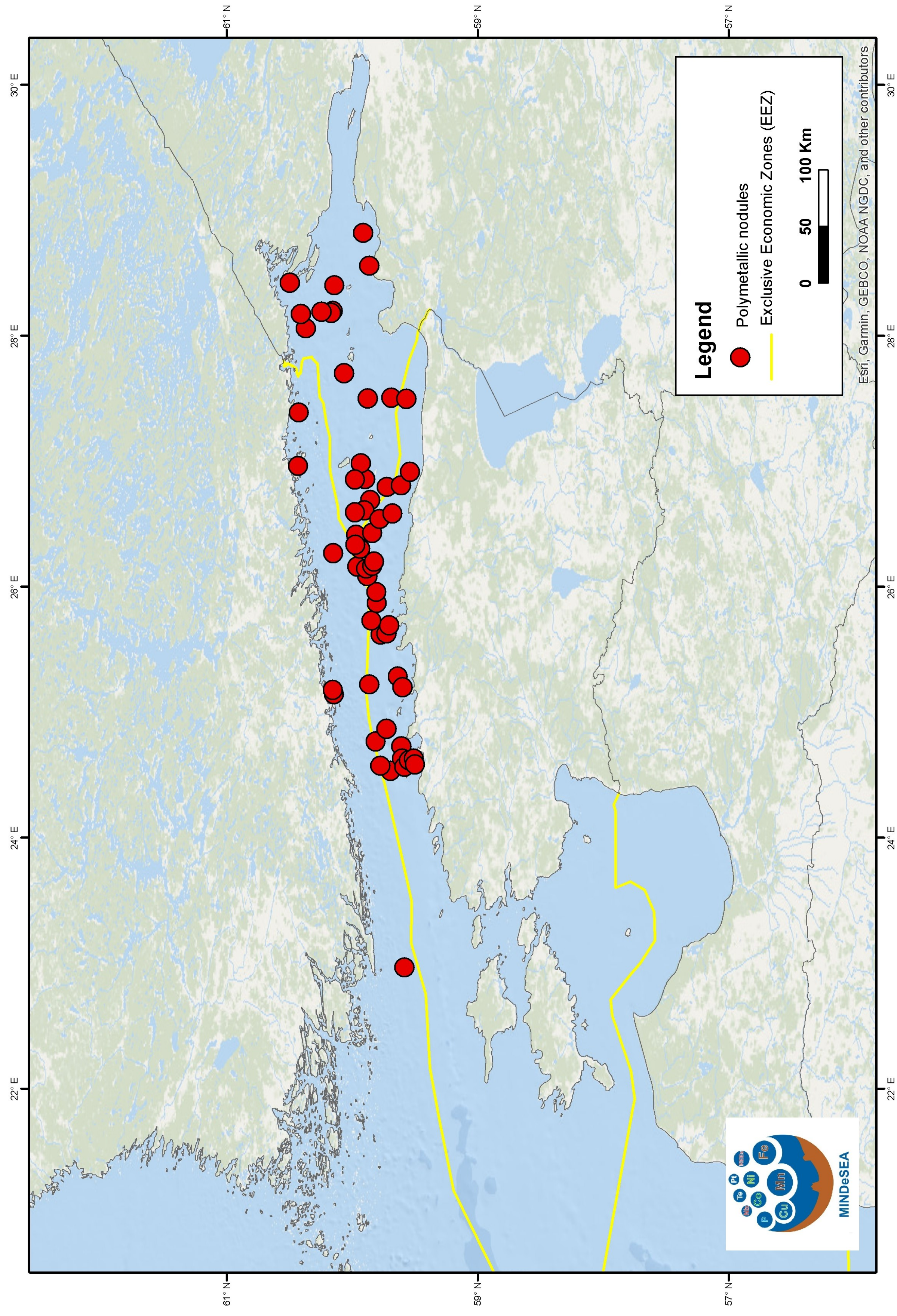

Figure 9. Spacial distribution of polymetallic nodules occurrences in the Gulf of Finland, compiled inside the MINDeSEA project.

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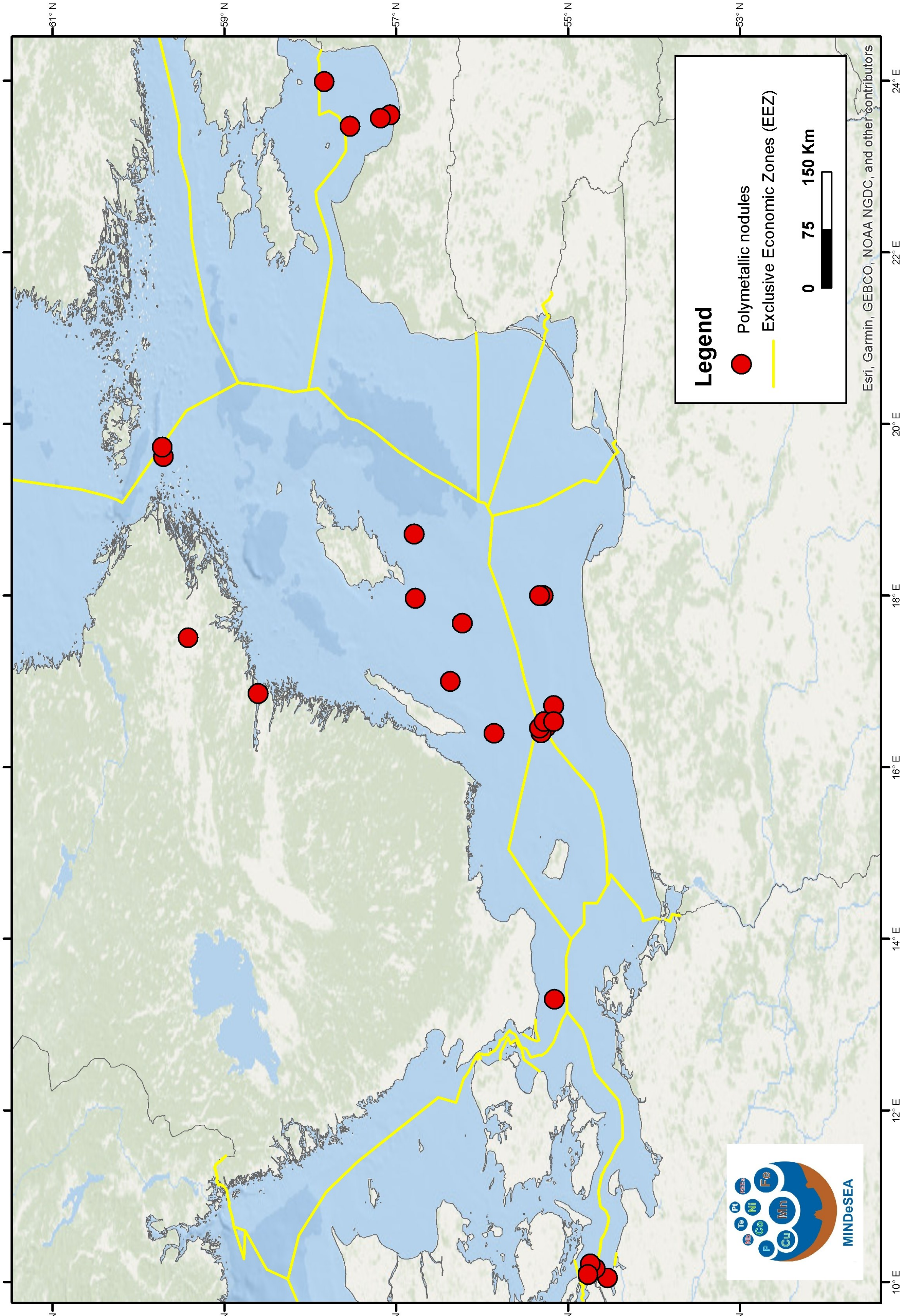

Figure 10. Spacial distribution of polymetallic nodules occurrences in the Baltic Sea proper, compiled inside the MINDeSEA project.

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tween ~650-750m, while the other subgroup of two sampling points are located deeper (~1200-1300 m depth). This bank constitutes a truly seamount, since the surrounding seafloor around it has depths greater than 5 km. The host rocks comprise different lithologies (sand, mud, schist, gneiss, limestone, granites, amphibolite) and have the same Paleozoic to Cenozoic ages. The nodules have an irregular and subspherical morphologies and their dimensions are between 1-5 cm.

A singular nodule occurrence exists ~120 km to the south from the previous group, much deeper (~4000 m depth) in an abyssal, undulated (there are some seamounts and hills in the surroundings) marine setting. The only available information concerns the host rock which is composed by sandstones and claystones.

Another occurrence is located in the Gulf of Cadiz (Cadiz-Contourite Channel), in the Hormigas Ridge, which is an ENE-WSW oriented elevated structure. Its corresponding depth is around 850 m, the nodules texture are banded/tabular and the host rocks correspond to Miocenic claystones and sandstones.

Finally, a group of three occurrences are linearly dispersed along a NW-SE orientation, from the Gulf of Biscay to the Celtic Sea. The corresponding depths vary between 500 m (the closest to the coast) and 4000 m in the Biscay abyssal plain. The sample positioned most offshore is located in a terrace (2500 m depth) existent in the lower part of the continental slope (Meriadzek terrace); Eocene calcareous lithotypes form the host rocks and the nodules are buried in sediment. The other two Gulf of Biscay occurrences have a significant variety of sedimentary rocks settings (sandstone, mudstone and limestone) covering the ocean floor basalt substratum. The nodules have a typical subspherical morphology.

2.3.3. Celtic Seas

MINDeSEA database identified five polymetallic nodule occurrences in these Marine Region. Four samples are located in Territorial Sea of Great Britain, very close from the cropped seashore and, consequently, at low depths (<50m), in an estuary setting. Two entries identified carbonate as host rocks and the nodules morphology having a spherical shape. The other occurrence is located in a distinct region, just outside Ireland EEZ and

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having completely different submarine physiographic characteristics. It is found in a typical marine abyssal setting (Porcupine abyssal plain), at 4420 m deep, very close (~20 km) from the base of continental slope (in Porcupine bank). The host rocks comprise clay and basalts. No further metallogenetic data is available.

2.3.4. North East Atlantic Ocean

There are 68 occurrences of polymetallic nodules for this Marine region of this MSFD (Marine Strategy Framework Directive). About 90% (corresponding to 61 points) of these occurrences are located in the Barents Sea; the rest is distributed in the following regions: four in the White Sea; two in the Rockall Plateau and a single point in the Greenland Sea. The majority of the occurrences (~77%) are located inside Russia, Norway and Denmark EEZ's.

Concerning the densest area of polymetallic nodules for this region, the Barents Sea, three major settings are identified: Marine (37%), Continental Shelf (22%) and Coastal Plain (4%). The MINDeSEA database has only 16 entries on water depth, ranging from 148 to 385 m. About 59% of the Barents Sea occurrences have associated data for the host rock type, and the majority are clay (70%), but sand and silt are also found as substrate sediment. The age of the host rocks spans from Triassic to Paleocene (Cenozoic). The most frequent age (corresponding to 42% of the available age data for this sea) is from the lower Cretaceous (Albian). The data information concerning the morphology and texture of the nodules are very scarce, corresponding to less than 5% of the occurrences listed.

The only nodule occurrence found in Greenland Sea, is located at about 1000 m depth, in a marine setting, inside the Denmark EEZ. It is situated about 20 km West from Kolbeinsey Ridge and 250 km East away from Greenland East coast. No other metallogenetic data is available.

The two nodule occurrences located westward of Celtic Sea, are outside any EEZ, in a marine setting, located on the Rockall Plateau, in a minor structure called Edoras Bank. The sampling depths are 1439 and 2301 m. The substrate rocks are basalt and chalk and geomorphologically they are located on the top of this bank flanks.

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Four nodule occurrences are found in the White Sea, very close from shore (< 45 km), in the Russia EEZ, continental slope setting. Host rocks comprise siltstone and mudstone, having very old ages of Neoproterozoic Era (Tonian and Ediacaran). Their sampling depths range from ~40 to 226 m (the deepest point is situated in the Gulf of Kandalakha).

2.3.5. Black Sea

In this region MINDeSEA database has listed 13 entries. One is located inside Romania EEZ and the rest of occurrences are inside Ukraine EEZ (4 points are included in the area corresponding to Territorial Seas). All occurrences are close to the coast and, consequently, their depths are always above 200 m. The host rocks are generally made by clay sediments and just one has been dated as belonging to Upper Pliocene. No further information is available for these occurrences.

2.3.6. Baltic Sea

This is the region having the highest number of registered polymetallic nodule occurrences in the MINDeSEA database, with a total number of 184 (one of these is located in a nonmarine environment, in the lake Malaren, in Sweden). For the Swedish area, at least, the registrations in the MINDeSEA database, are where a high frequency of nodules have been found. For a clear analysis of the data, the Baltic Sea is subdivided in three sub regions: Gulf of Finland, Gulf of Bothnia and Bothnian Sea and Baltic proper (this subregion includes the Gulf of Riga and the Kiel Bay). The distribution of the registered nodules occurrence in these sub regions is illustrated in Figures 7-10. The largest amount of registered data is present in the Gulf of Bothnia and Bothnian Sea (54% of the Baltic Sea total) (Figure 11a). The data distribution considering the EEZ's of the Baltic countries is showed in Figure 7, where it is possible to observe that the largest amount of registered nodule occurrences is located in Sweden EEZ (54% of all the Baltic countries EEZ) (Figure 11b). This is probably mostly due to the registration of samples in the MINDeSEA database and not to real occurrence. Observations from, for example, scientific diving and drop cameras show that polymetallic nodules are observed in 6831 locations in all basins of the Finish part of the Baltic Sea, with the exception of the southern Bothnian

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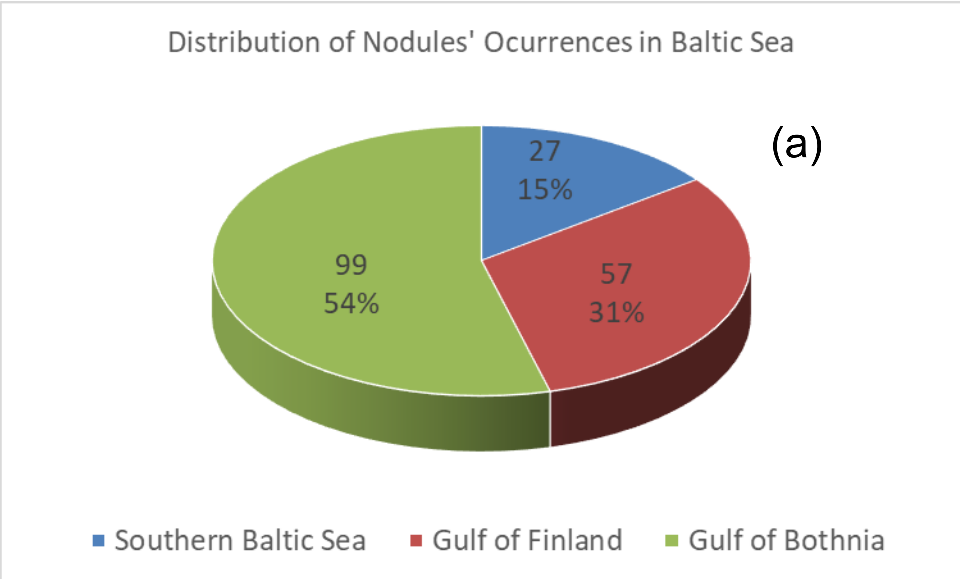
Sea (data from the Finnish Inventory Programme for the Underwater Marine Environment (VELMU) MapService: paikkatieto.ymparisto.fi /VELMU_mapservice/). The most abundant deposits in Finnish waters are reported from the Gulf of Finland and the Kvarken area in the Gulf of Bothnia. These mineral deposits are observed in depths of 0–75 m, spanning different seafloor types from muddy bottoms to rocky seafloors. In the northern parts of the Finish part of Gulf of Bothnia, concretions are generally observed in shallower



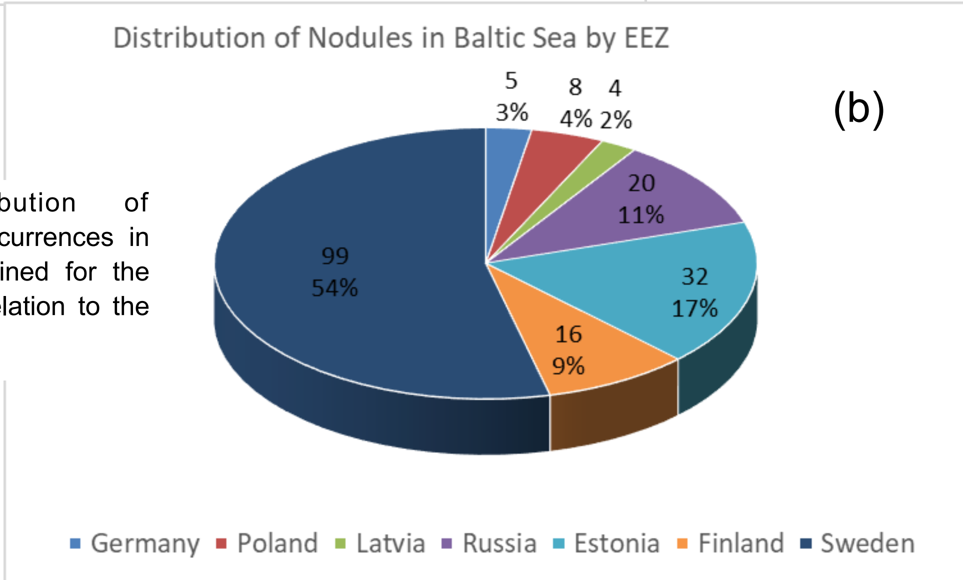


Figure 11. Distribution of polymetallic nodules occurrences in the three subareas defined for the Baltic Sea (a) and in relation to the EEZ Baltic countries (b).

depths (<25 m) than in the southern parts (Kaikkonen *et al.*, 2019).

Concerning the depths of the registered nodules' occurrences in the MINDeSEA data-

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base, 130 out of 131 existent data are in the range of 13 to 143 meters (the other data point, located in Bothnia Sea, is 256 m deep); however, it must be noted that ~55% of depth data are included in the range of 40 to 80m water depth (Figure 12a). When considering the three sub regions defined separately (Figure 12b,c,d), it can be seen the lack of significant depth differences among them (the only remark to be done is the smaller depths observed for the Baltic Sea Proper, whereas the majority of the data is located between 20 and 60m water depth, but this could be only due to the presence of a smaller number of datapoints).

The geomorphologic information associated to the polymetallic nodules occurrences in the database are very scarce and, thus, if there is a correlation it is not found there. However, concretion fields seem to occur more frequently on slopes and on edges of larger depressions in the Gulf of Bothnia and Gulf of Finland (Kaikkonen *et al.* 2019).

In respect to the nodules morphology, four distinct shapes are identified: spheroidal (26 datapoints), spheric/rounded (19), disc/flat (12) and ring (6); however, it must be noted that most (~65%) of the nodules occurrences don't have any morphology description associated.

Host rock information is available in about ~2/3 of the occurrences in the Baltic Sea; the lithotypes identified are very diversified and include post glacial sediments (clay, silt or sand) over a diversified glacial sediment types (mainly clay in dimension) which, together with glacial clays, dominate the host rock (both types comprising almost of 50% of the available data). Other lithologies identified include carbonate sediments, mudstones, siltstones, sandstones, metamorphic and igneous rocks.

Regarding the age of the host rocks, it can be observed that all Erathems of the Phanerozoic are represented in MINDeSEA database, including ages from Cambrian to the Quaternary periods, this last clearly dominating. Considering the Quaternary, most of the age data are from Holocene (50 data depths) and 13 correspond to Pleistocene, which is in agreement with the glacial and post-glacial types of sediments. The older ages observed, belonging to the Precambrian (meso and Neoproterozoic) are associated with igneous and metamorphic rocks.

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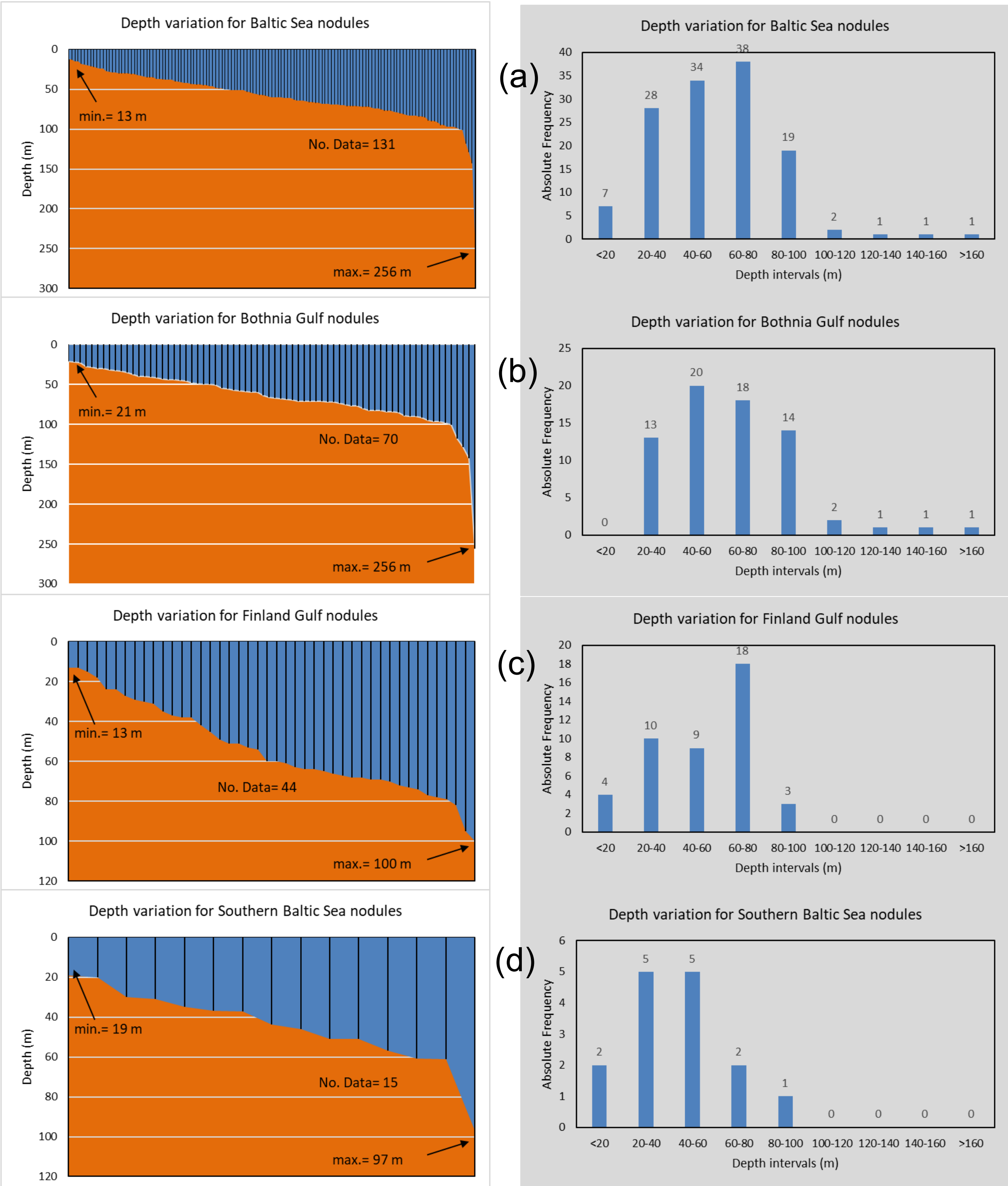

Figure 12. Depth variation (figures on the left) and absolute frequency histograms (figures on the right) of depth intervals for polymetallic nodules occurrences in all the Baltic Sea (a) and in its subareas: Gulf of Bothnia (b), Gulf of Finland (c) and Southern Baltic Sea (Baltic Sea proper) (d). Each vertical black line on the left figures represents a nodule occurrence.

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2.3.7. International Waters (AREA)

Four distinct locations having polymetallic nodules are identified in international waters in Atlantic Ocean (Figure 5). One occurrence is located West of MAR near Atlantis Fracture Zone, at about 3500 m water depth, in a calcareous ooze host sediments. Six other occurrences are positioned close Kane fracture zone at depths between 5000 and 5500m. While some nodules are found within the sediments, others on the sediment surface. This sediment is clay covering gabbros and serpentinites. Spheroidal and reniform morphologies are identified for the nodules. Finally, five occurrences are found in the Madeira Abyssal Plain, NE of Great Meteor Seamount, at depths between 5200-5300 m. The host rocks are calcareous ooze and red clay of Cretaceous age. A significant variety and amount Polymetallic nodules were identified for this area.

2.4. Polymetallic nodules occurrences – geochemical data

To illustrate the geochemical variability of the polymetallic nodules compiled in the MINDeSEA database, we selected three main type of graphs: 1) $Fe_2O_3^T$ vs. MnO (in wt% for both elements) - this graph is the one that present the higher number of data points in all geographic regions and sub regions defined; 2) Co vs. Ni+Cu (in wt% for all these elements); 3) Chondrite normalized REE concentrations. The analysis of this graphs allows to have insights about the genetic processes of the nodules.

Furthermore, geochemical data were plotted in the ternary diagram of Bonatti *et al.* (1972) and in two binary diagrams based on the REY contents in order to better interpret their genetic process (Bau *et al*., 2014).

The data available for the Macaronesia is very scarce due to the conjunction of a small number of samples and scarceness of geochemical analytical data. Iron concentrations (~22-27 wt%) are slightly higher than those of Mn (15-19 wt%) (three analyses), whereas the single Co-Ni-Cu analysis show low concentrations in these three elements. No data is reported for the REE. Globally, the geochemical compositions are similar to the nodules formed by hydrogenetic processes in the Indian and Pacific Oceans.

The data for three regions - Bay of Biscay and the Iberian Coast, Celtic Seas and NE At-

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lantic Ocean – is shown in Figures. 13 and 14. The majority of the data are richer in iron, comparatively to manganese, but six samples have higher Mn/Fe>5. When observing the relationships among Co-Ni-Cu, only the two nodule samples from Bay of Biscay and the Iberian Coast present significant high concentrations for these elements, suggesting a diagenetic contribution for their formation. Considering the REE data, only one sample, from the NE Atlantic Ocean, have a significant total amount reaching ~0.16% (Ce is the most element contributor to this high REE^T).

When considering the Black Sea and International Waters (here grouped in the same graph just to avoid a large number of individual graphs having low data points) (Figures 15 and 16), all the data points are clearly enriched in Fe comparatively to Mn (however the AREA samples have a higher Mn/Fe). Conversely, Ni+Cu have higher concentrations in the Black Sea and these are ~2.5 to 3 times higher than Co. Total REE concentrations are low for all the Black Sea nodules, but the single REE analysis from the AREA, located in the Madeira abyssal plain show a significant REE^T (0.21 wt%), whereas the light REE are significantly enriched to the heavy REE.

Finally, the geochemical data for the Baltic Sea was divided into three sub regions: Gulf of Bothnia (including Bothnian Bay) (Figure 17), Gulf of Finland (Figure 18) and Baltic Sea proper (Figure 19). All polymetallic nodules in all these three sub regions have clearly Mn/Fe ratios below 5 and no clear difference exist among them; however, the highest Mn concentrations (as well the number of nodules having MnO > 30 wt%) are observed in the Baltic Sea Proper. The nodules from the Gulf of Finland are the ones showing a clearer inverse correlation between manganese and iron. The nodules from Gulf of Bothnia and the Baltic Sea Proper show similar correlation and concentrations in Ni+Cu vs. Co; however, in both regions, the highest values for these elements are relatively low (Ni+Cu<0.09 wt%; Co<0.05 wt%; however, there is a general tendency for the highest values of these elements be present in the nodules from Gulf of Bothnia). Considering the REE data, all nodules from the Baltic sea have light REE enriched patterns, comparatively to heavy REE; the total REE concentrations for almost all nodules are <280 ppm, however three samples show higher values (366, 471 and 720 ppm).

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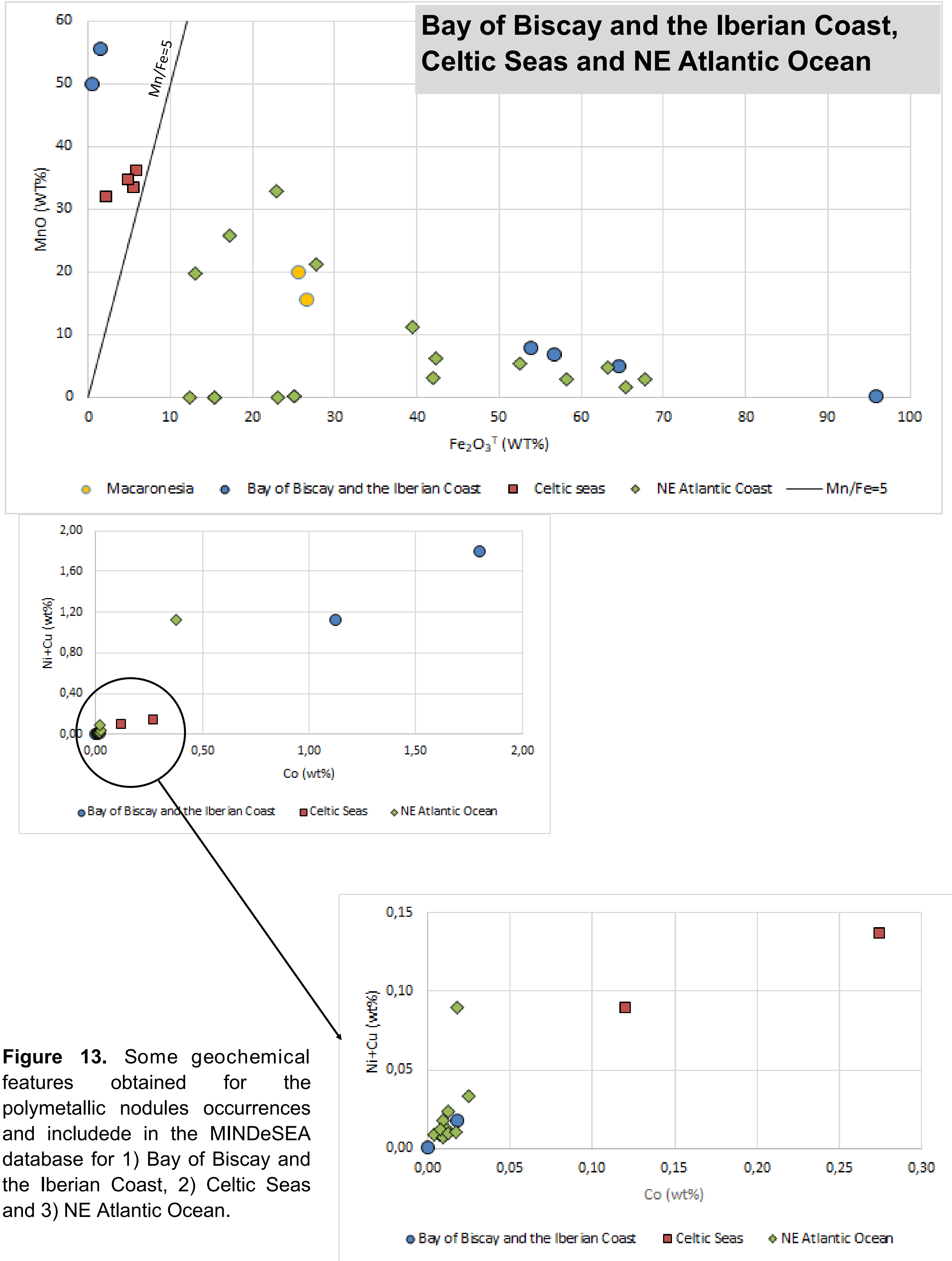

Figure 13. Some geochemical features obtained for the polymetallic nodules occurrences and includede in the MINDeSEA database for 1) Bay of Biscay and the Iberian Coast, 2) Celtic Seas and 3) NE Atlantic Ocean.

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Bay of Biscay and the Iberian Coast, and NE Atlantic Ocean

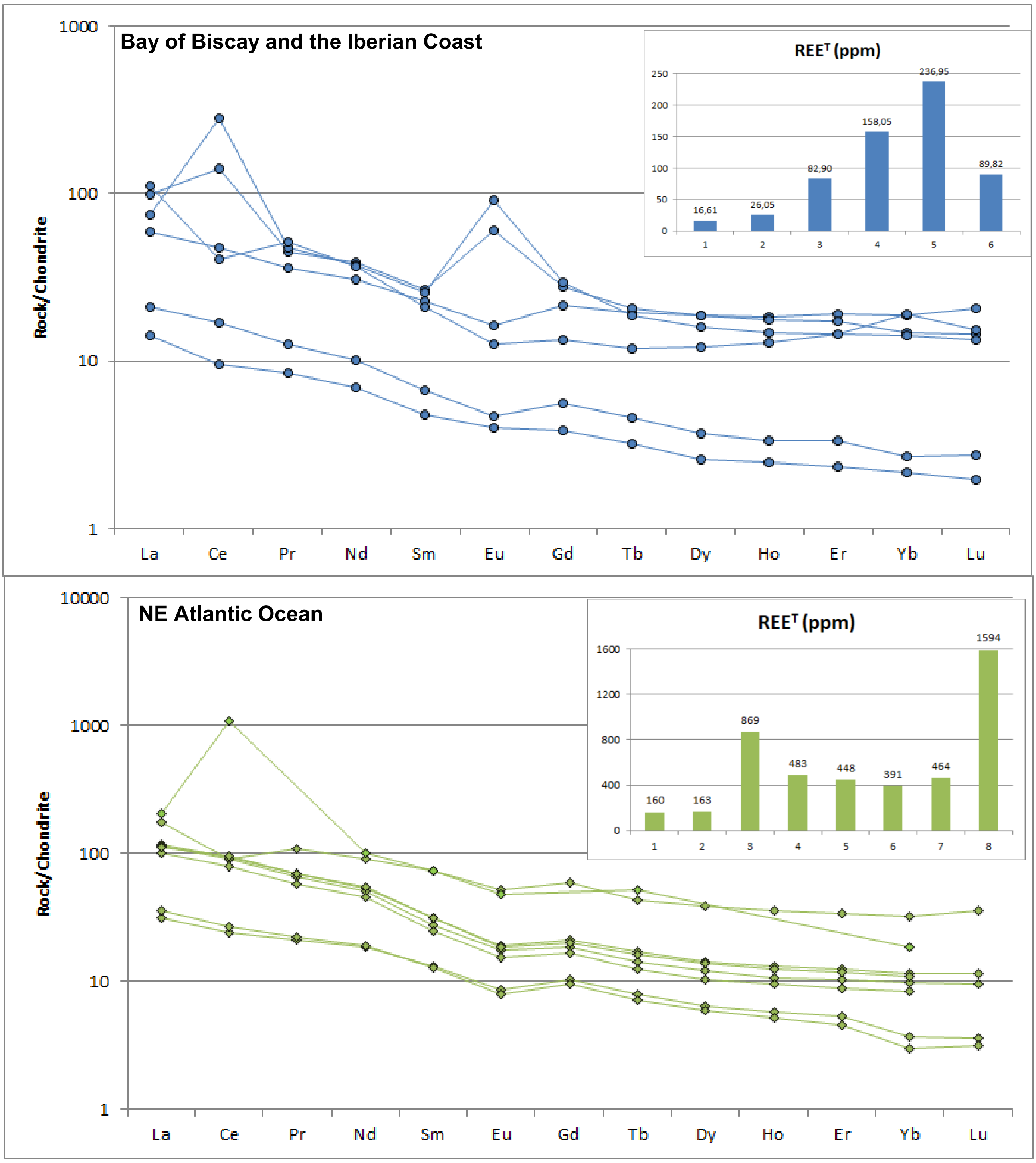

Figure 14. REE chondrite normalised concentrations obtained for the polymetallic nodules occurrences and includede in the MINDeSEA database for Bay of Biscay and the Iberian Coast and NE Atlantic Ocean.

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Black Sea and International Waters

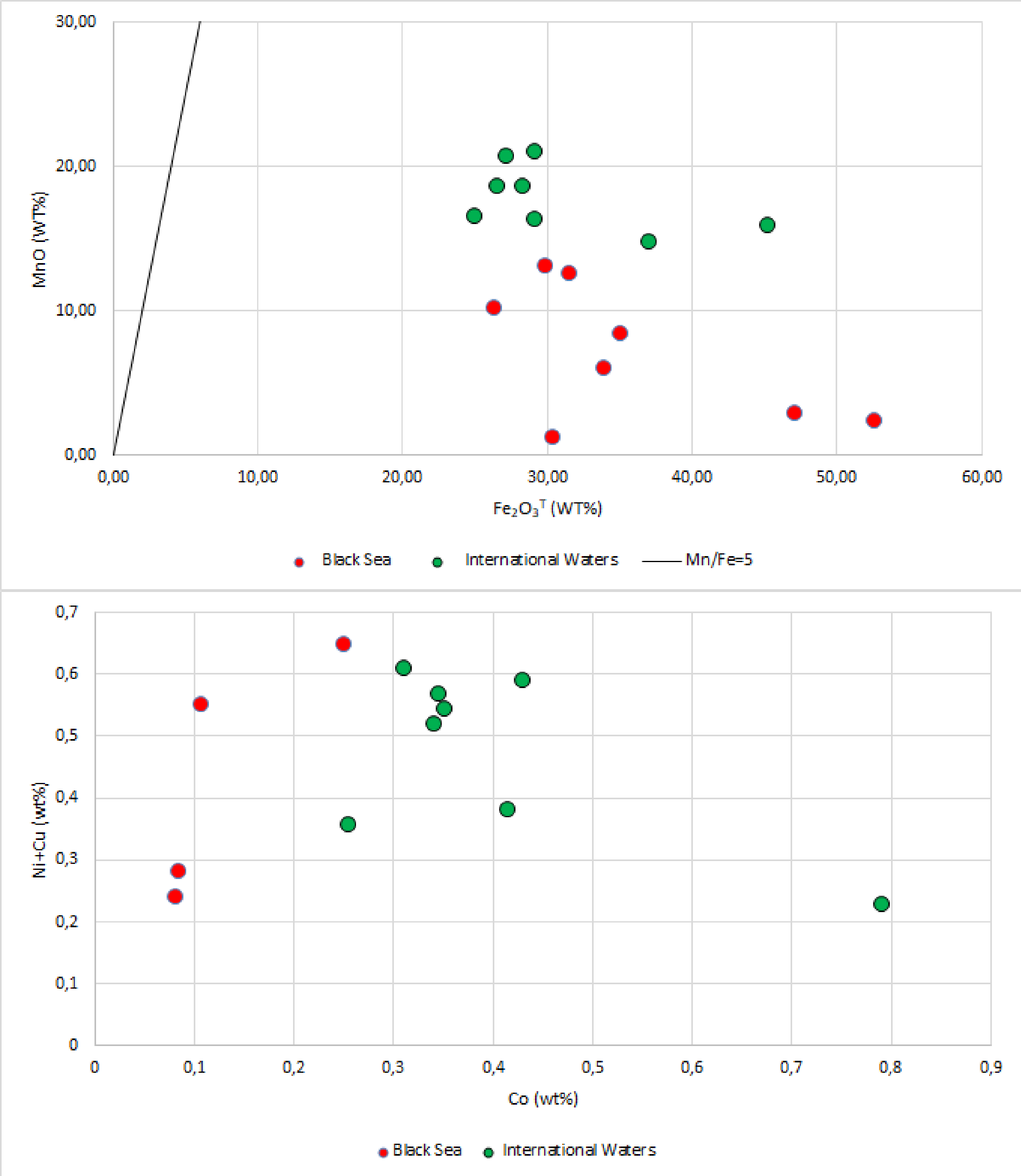

Figure 15. Some geochemical features obtained for the polymetallic nodules occurrences and included in the MINDeSEA database for 1) Black Sea and 2) International Waters.

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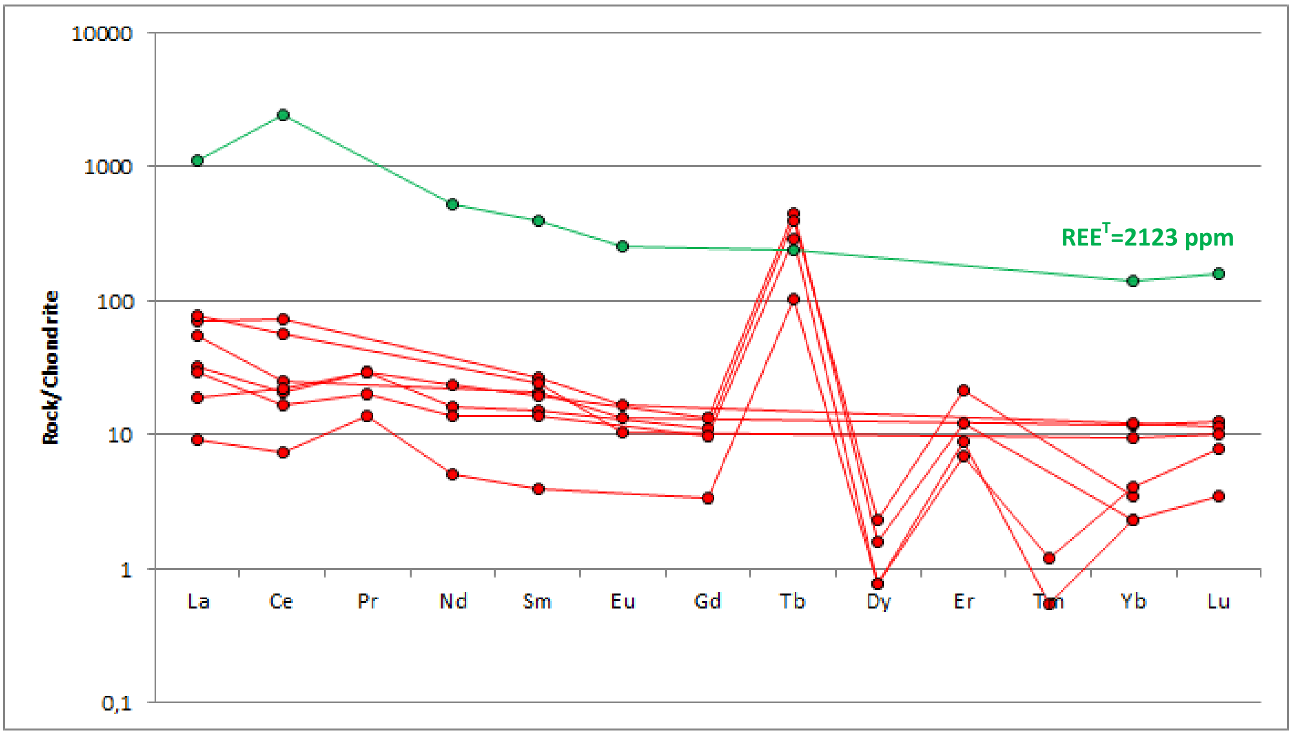
Black Sea and International Waters



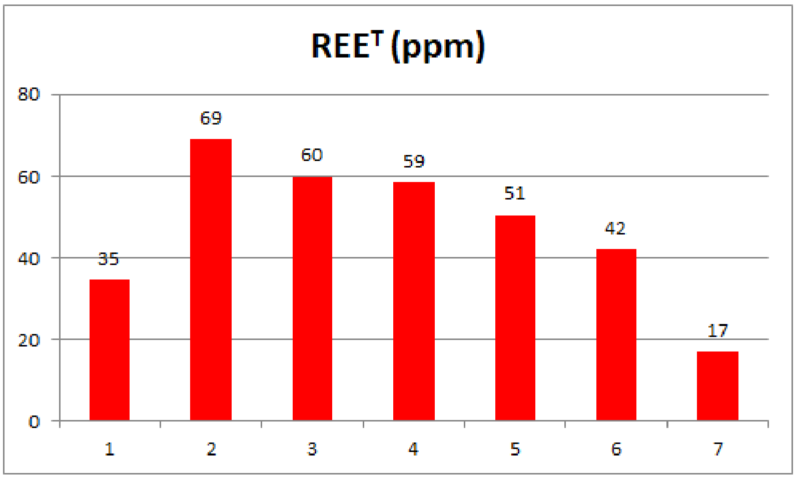


Figure 16. REE chondrite normalised concentrations obtained for the polymetallic nodules occurrences and includede in the MINDeSEA database for 1) Black sea (red points and lines) and 2) International Waters (green points and line). Histogram refers to the total REE concentrations for the Black Sea.

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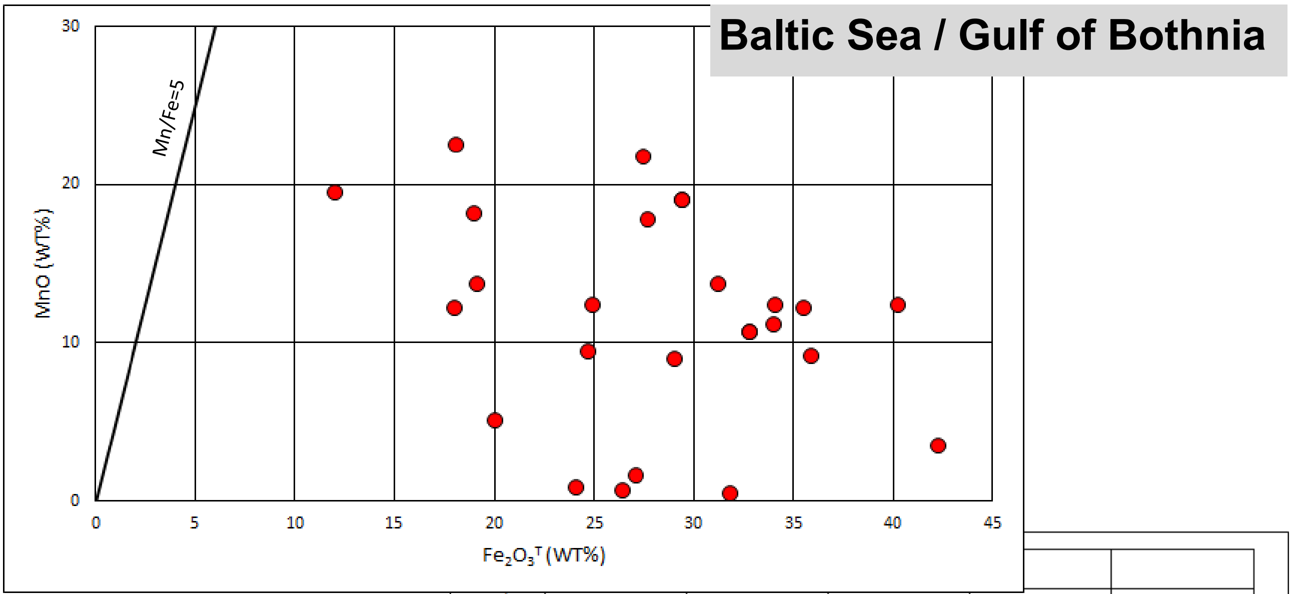


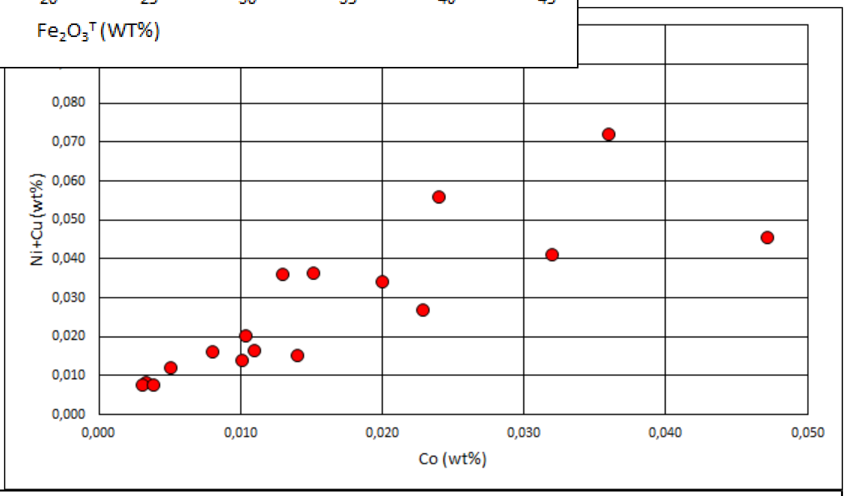
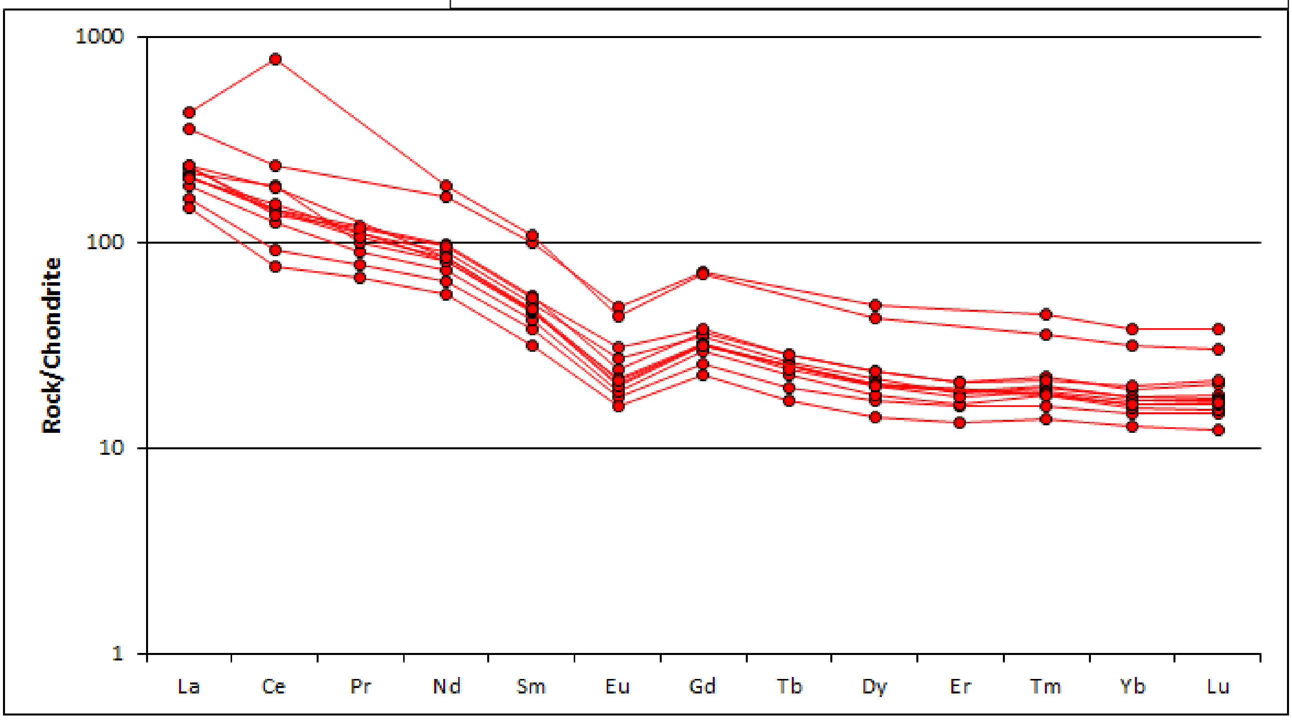


Figure 17. Some geochemical features obtained for the polymetallic nodules occurrences and included in the MINDeSEA database for Gulf of Bothnia (Baltic Sea)



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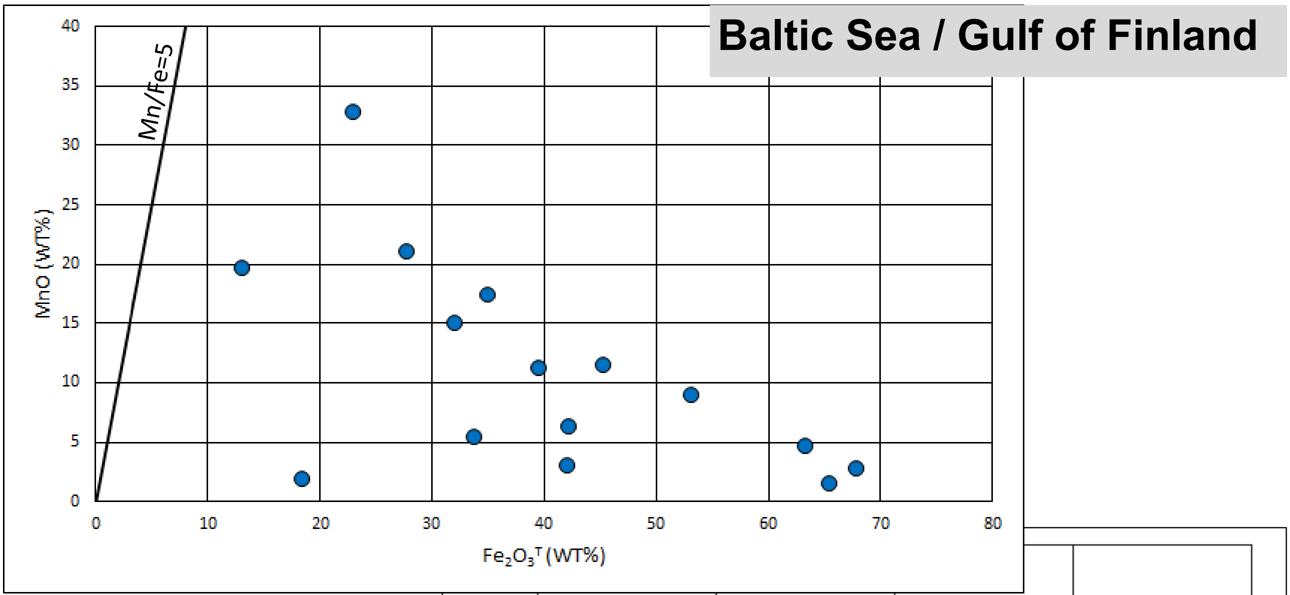


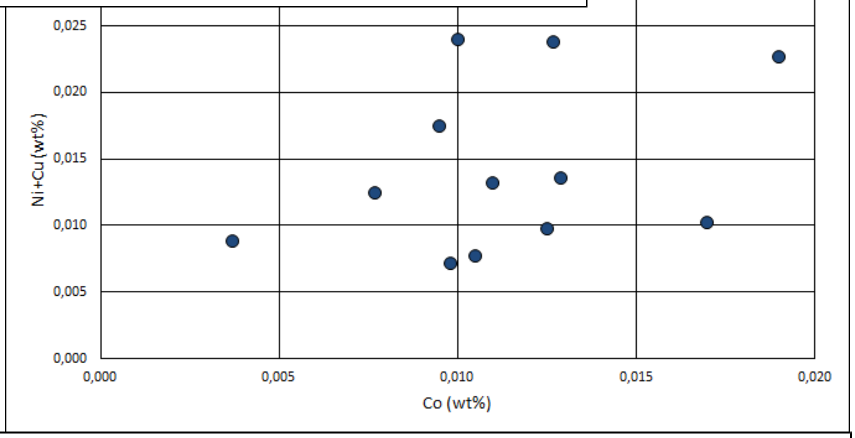
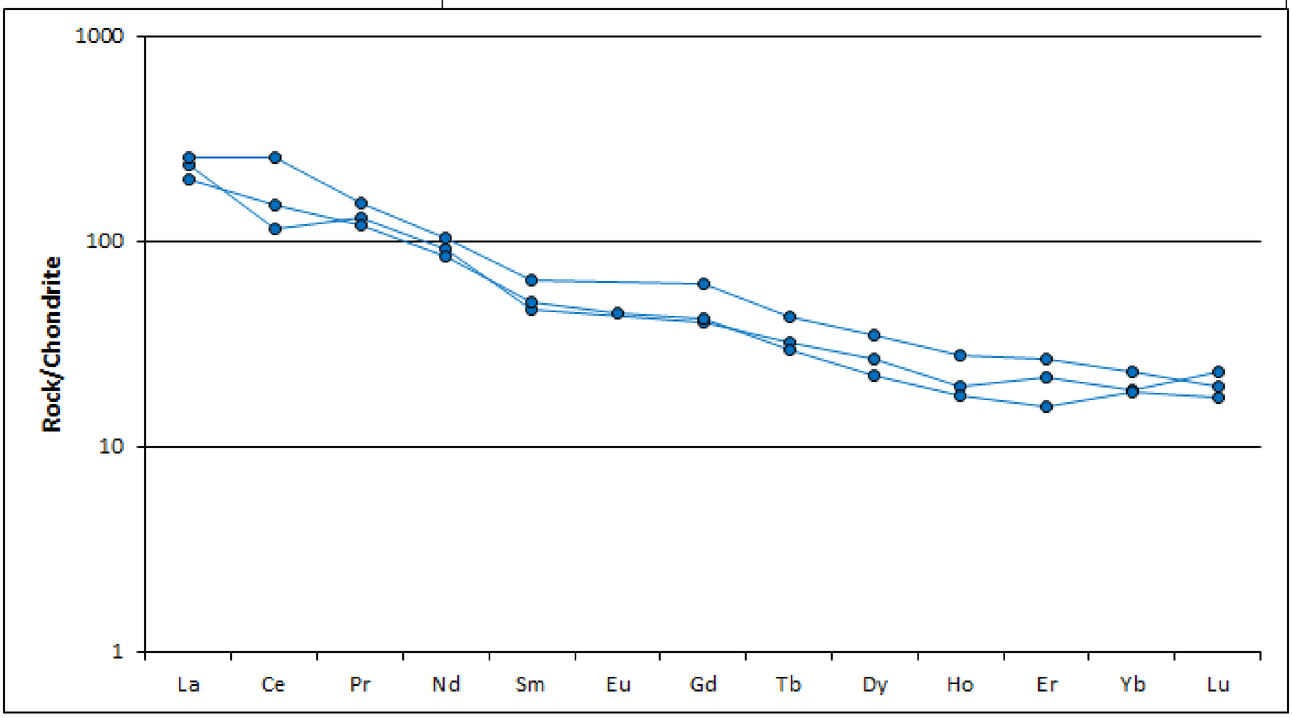


Figure 18. Some geochemical features obtained for the polymetallic nodules occurrences and included in the MINDeSEA database for Gulf of Finland (Baltic Sea)



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Baltic Sea / Baltic Sea proper

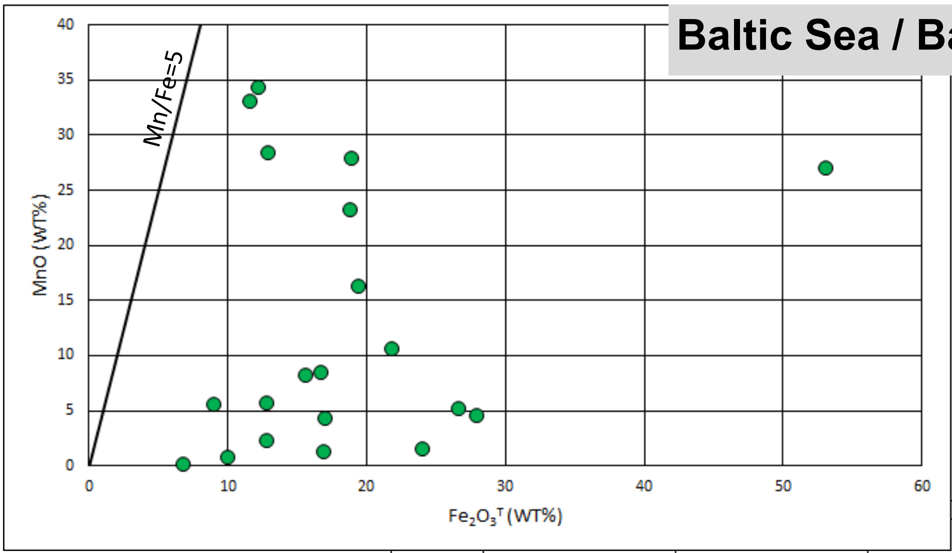
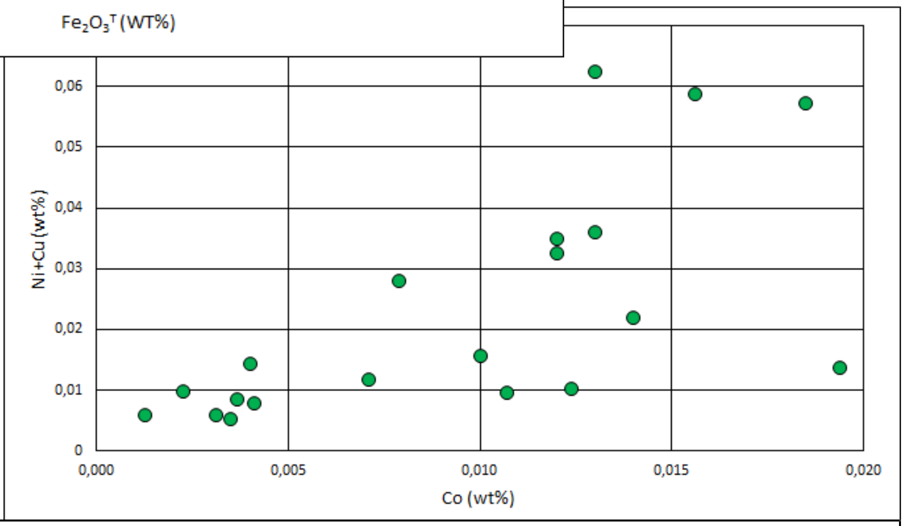
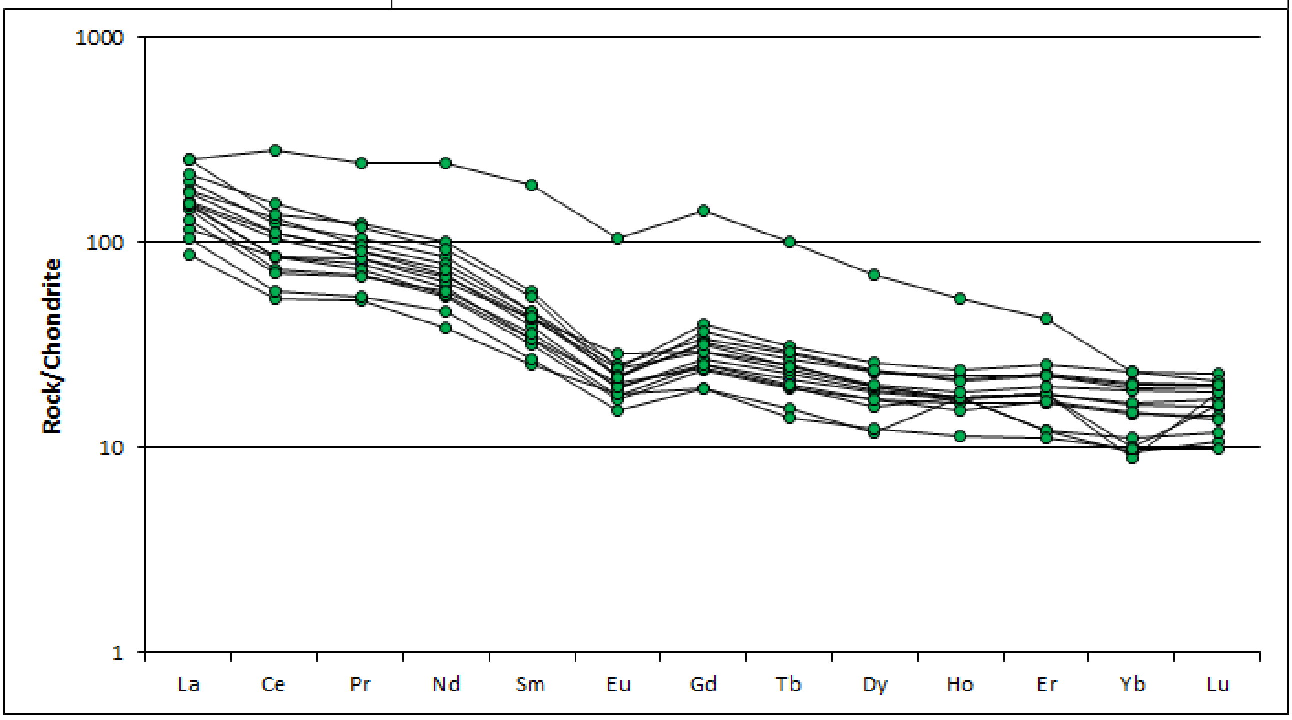


Figure 19. Some geochemical features obtained for the polymetallic nodules occurrences and included in the MINDeSEA database for Baltic Sea proper (Baltic Sea)





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According to the ternary diagram (Bonatti et al., 1972) nodules from the Edoras Bank and Loch Fyne, localized in the North East Atlantic Ocean, show two main genetic processes, hydrogenetic and diagenetic, with some sample localized in the mixed region (Figure 20). Nodules from the Kane fracture zone and the Great Meteor, in the international waters, plot in the hydrogenetic field, showing high contents in Ni+Cu+Co typical of a slow growth (Figure 20). In The Galicia Bank area, localized in the Bay of Biscay and Iberian Margins region, nodules show a dominant diagenetic origin, with great contents of Mn or Fe and a some hydrogenetic and hydrothermal influence, the latter from geothermal fluids (Figures 20 and 21a,b) (González *et al.,* 2016). Finally, Fe-rich nodules both from the Baltic sea and Gulf of Bothnian seems to have a hydrothermal origin, according the ternary diagram (Figure 20), while using the binary diagram of the REY indexes is evident a general diagenetic origin (Figure 21a,b). Same behaviour can be seen in nodules from the Hormigas Ridge in the Gulf of Cadiz. These nodules also present a hydrothermal influence due to the presence of a series of mud volcanoes in the area (Figures 20 and 21a,b). Nevertheless, the Bonatti diagram is very useful in abyssal plain domain, but the shallow water nodules located in continental crust, like those occurring in the Gulf of Cadiz or the Baltic Sea, should be analysed using different approaches. Most of them were formed by diagenetic processes with minor influence of hydrogenetic processes or geothermal influence (González *et al.,* 2009; 2012).

3. Final Remarks

1. With this report we have identified from published studies a group of parameters that are considered to promote the formation of polymetallic nodules, and which are also used as a basis for defining prospective areas for seafloor exploration (1.5. Environmental parameters favouring the formation of polymetallic Nodules)

2. However, all these parameters were based on studies made in the most important and well-known polymetallic nodule fields that are located in the Pacific and Indian oceans.

3. MINDeSEA data compilation have identified 296 polymetallic nodules occurrences in the European seas. The majority of these registrations is located in the Baltic Sea (184 occurrences, corresponding to 62% of the total) followed by North East Atlantic Ocean (in

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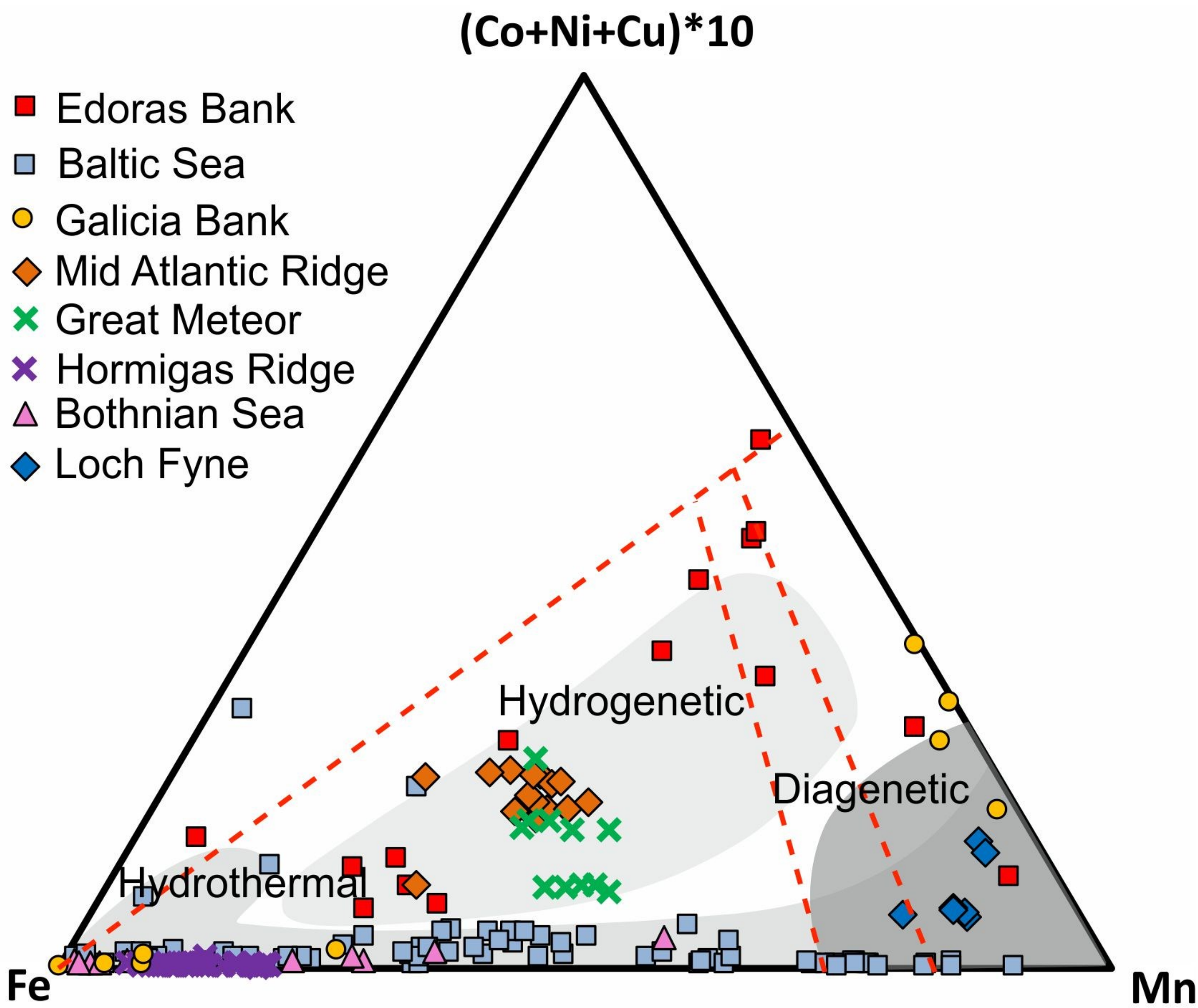

Figure 20. Relationship among Co+Ni+Cu, Fe and Mn, for polymetallic nodules registered in MINDeSEA database (ternary diagram from Bonatti *et al.,* 1972).

which was included some data points that are geographically inside the Arctic Sea), having 68 identified occurrences (23% of the total). The remaining occurrences (15%) are distributed through other five marine regions/sub regions – Macaronesia, Bay of Biscay and the Iberian Coast, Celtic Seas, Black Sea and International Waters (AREA).

4. A comparison of the geographic, submarine and geotectonic settings between those that occur in well-known Pacific and Indian ocean nodules fields and those that characterize the regions where the nodules occurrences were identified in this MINDeSEA project,

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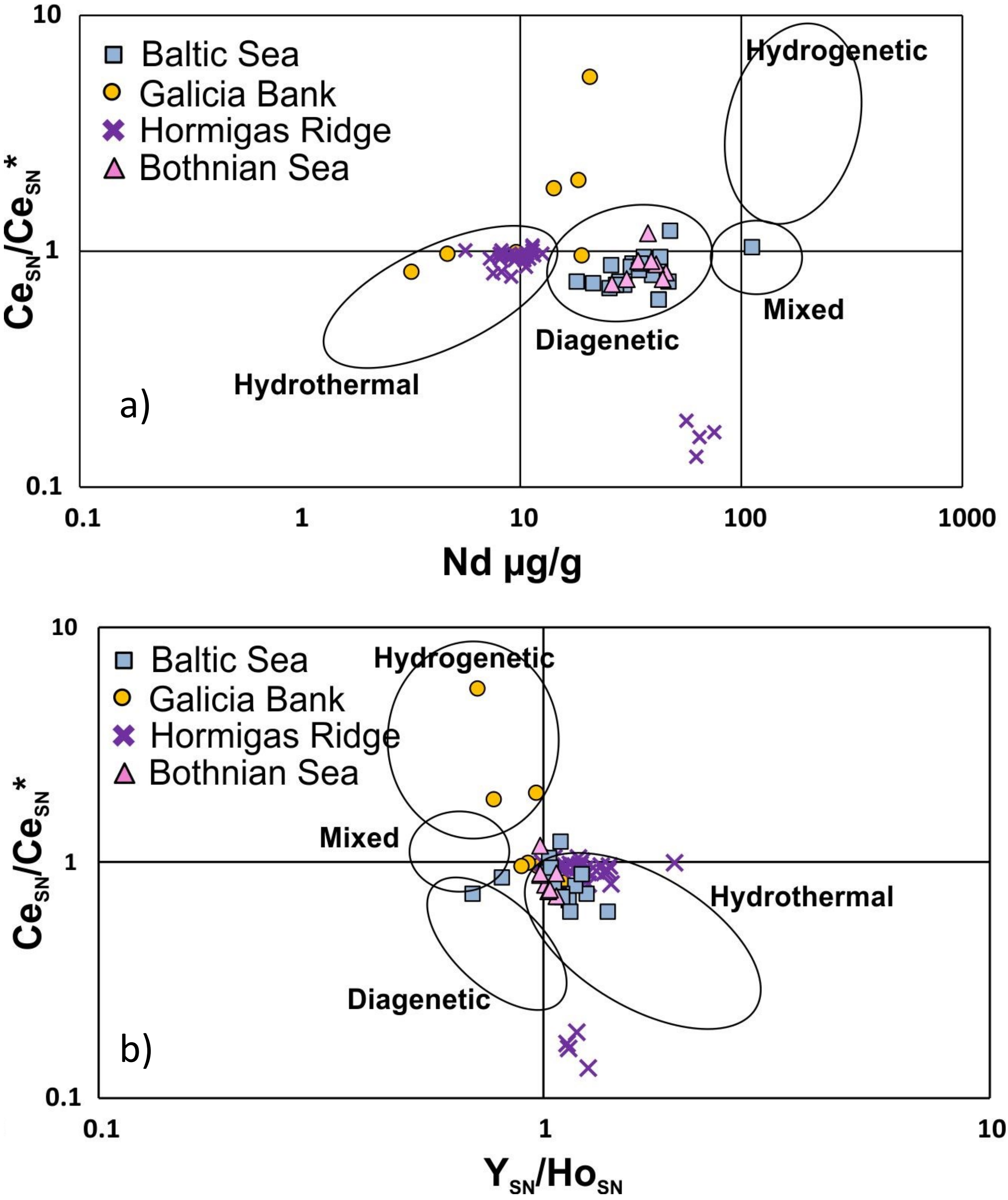

Figure 21. Relationship among some of the rare earth elements (Ce, Nd and Ho) and Y, for polymetallic nodules registered in MINDeSEA database. a) Ce_{SN} /Ce^*_{SN} *vs* Nd and b) Ce_{SN}/ Ce^*_{SN} *vs* Y_{SN}/Ho_{SN} (Bau *et al.,* 2014). Subscript SN stands for Post-Archean shale normalized

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allows us to identify only two regions having “similar” settings – the abyssal plains located inside Macaronesia and those, contiguous but outside this region, found in International Waters.

5. The limited number of nodules occurrences in Macaronesia and in International Waters and the insufficient metallogenetic data available only allow us to assume that prospect evaluation parameters would be identical to those defined for the nodules fields in the Pacific and Indian oceans. Additionally, through the identification of polymetallic nodules covering vast areas of the summit of the Tropic Seamount (about 30 samples of polymetallic nodules were collected during the James Cook cruise in 2016 (Murton *et al.,* 2017), but no mineralogical or geochemical data are yet available) it is reasonable to assume that they growth under the same main hydrogenetic origin with some influence of diagenetic and/or hydrothermal processes during their formation (Marino, 2020). In this way it is assumable that the main mineralogy is represented by vernadite (with less birnessite and diagenetic asbolane, buserite and todorokite) and goethite group minerals. Diagenetic minerals could grow in periods when nodules were completely covered by sediments and in suboxic conditions. The main geochemistry dominated essentially by Mn and Fe with variable contents of other trace metals in which the greatest contents are represented by Co, Ni, Cu, V, Mo, Te, PGEs and REY depending on the grade of influence of the different genetic processes (Marino *et al.*, 2017; 2018; 2019).

6. Baltic Sea occupies a relatively small shallow water and confined area, whereas the strong inputs of river water, the topographic succession of sills and basins, and the narrow entrance to the North Sea are the main features that determine the hydrography of the Baltic Sea (Schneider & Müller, 2017). Relatively high nodule abundances between 10 and 40 kg/m^2 occur in the gulfs of Riga, Finland, and Bothnia in water depths between a few tens of meters and about 250 m, covering areas of a few hundred km^2. This abundance is related to the large input of Mn- and Fe-rich suspended matter through rivers in the northeast and east (Gulf of Bothnia, Gulf of Finland) and the formation of an oxidized layer in the upper 2–15 cm of the sediment column (Glasby *et al.* 1997). Fast-growing Fe-Mn concretions are mainly found in the western Baltic Sea, their formation being related to the development of summer anoxia and the diagenetic mobilization of Mn. In addition to the completely different geographical, oceanographic and geological settings, com-

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pared to the Pacific and Indian Oceans, the trace metal content of the polymetallic nodules from the Baltic Sea are generally lower than in nodules from the open ocean (Kuhn *et al.*, 2017). No specific metallogenetic parameters are identified in MINDeSEA database favouring the formation of the nodules in Baltic Sea.

According to Kaikkonen *et al.*, 2019 there is a correlation between phosphorus concentration and occurrence of nodules, which may explain why nodules are common in slope areas that are bordering deeper basins, from which phosphorus is released under anoxic conditions. Nodules mainly occur in oxic sea areas and are dissolved under permanent anoxia.

However, phosphorus does not necessarily directly drive nodule growth because high phosphorous concentrations are correlated with high concentrations of other dissolved elements in bottom waters. So, phosphorus may act as a proxy for the availability of other elements (Kaikkonen *et al.,* 2019). This has resulted in nodules forming distinct belts on the fringes of deeper basins that span hundreds of kilometers within the Gulf of Bothnia, Gulf of Finland and Baltic proper in Swedish, Finnish, Estonian and Russian territorial waters (EMODnet Geology, 2019).

The abundant nodule occurrence in all different basins and water depths in the Baltic Sea suggests variable processes of nodule formation depending on their environment of formation. The chemical characteristics of the underlying sediment are likely also important to the formation and metal content of nodules (Zhamoida *et al.*, 2017). These data are unfortunately less common. The most abundant Mn-rich spheroidal nodule fields are found within areas where Precambrian crystalline rocks (Baltic Shield) form the basement since these rocks are rich in Mn and Fe. Glacial till formed from fragments of these rocks has been proposed as also a source of Mn and Fe in these concretions. However, many observations of nodules are related to finer grained sediments clay/silt sediments, both older (glaciolacustrine) and newer (postglacial) deposited. Glacial clay is often covered by a residual of thin layers (2-30 cm) of mixed sediments (mainly silt, sand, gravel and cobbles). From observations, there are also some qualitative indications that larger nodule occurrences on the seabed are associated with older sediments and an environment that is neither to erosive and mobile or accumulating. This may result from the fact that this is

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an environment that have permitted the nodules to form and grow during longer time.

In more recent (postglacial) deposits, when the nodules are not exposed on the seabed, they have also been found covered by silty-clay muds. In these cases, they are often spheroidal. In general, the abundance of nodules and the Mn contents increase within increasing water depth as a result of more active processes of Mn mobilization and migration in the anoxic environments encountered at the deepest basins of the eastern Gulf of Finland (Zhamoida *et al.*, 2017). Within the same area, the manganese concentration of the spheroidal concretions depends on the size of the concretions. The larger concretions sampled at one site have higher Mn and lower Fe concentrations than smaller ones (Zhamoida *et al.*, 2017)

In the model run by Kaikkonen *et al.*, 2019 depth was found to be the most influential predictor in the concretion models, followed by total phosphorus, occasional hypoxia, frequent hypoxia, and depth-attenuated wave exposure. Salinity, chlorophyll a, nitrogen, and ruggedness had smaller influences on the occurrence of nodules throughout the models.

7. A similar situation to the Baltic Sea is identified in the Black Sea (no additional information was found).

8. The geographic, oceanographic and tectonic settings present in the Bay of Biscay and the Iberian Coast are quite distinct; in this region some (few) nodules occurrences are identified in the western Galicia continental margin and in the Gulf of Cadiz. The metallogenetic information available for these two cases have allowed to assume that their generation is controlled by local conditions.

In the western Galicia continental margin, the polymetallic nodules occur together with extensive phosphorite pavements on seamounts and banks existent there (González *et al.*, 2014, 2016). The formation of these nodules and phosphorites is at least partly related to the activity of deep-reaching faults and the geothermal mobilization of metals from a deeper crustal reservoir (González *et al.*, 2014, 2016).

In the Galicia Bank area, two main types of nodules (Mn-rich and Fe-rich) can be found, having growing histories under the influence of different genetic processes:

- Mn-rich nodules are formed by the combined action of diagenesis and hydrothermal

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processes, the latter due to tectonic movements that could have provided the geothermal heat in order to remobilize the elements producing metal enriched hydrothermal fluids (ENADIMSA, 1980; González *et al.,* 2016). The main mineralogy is represented by todorokite, romanechite, and coronadite that are different type of diagenetic Mn oxides with a strong 10 Å reflection. These nodules are enriched in Mn (between 39 and 45 wt%) and also show the enrichment of several strategic elements and critical raw materials (CRMs) as Co, Ni, Cu, Mo, Pb, V and Tl. On the other hand, REYs have low contents (between 140 and 400 ppm) and their normalization to the PAAS show a positive Eu anomaly that also confirm the hydrothermal influence during their growth (González *et al.,* 2016; MINDeSEA, 2021).

- Fe-rich nodules, formed essentially by the precipitation of goethite minerals around a nucleus showing very high contents of Fe (between 29 and 67 wt%) and a Mn/Fe ratio between 0.03 and 0.09. These nodules are brown to yellowish coloured and are formed under the main influence of diagenetic processes, resulting in fast growth rates and low contents of any trace metals (Co, Ni, Cu, Mo, etc.) and REY (total contents less than 0.1 wt%). The slightly enrichment in some elements as V, Ba and As, also suggests a low hydrothermal influence, due to geothermal fluids input, during their formation (ENADIMSA, 1980; González *et al.,* 2016).

In the Gulf of Cadiz, the nodules' formation is related to hydrocarbons seeps, mud and evaporitic diapirism, and the activity of strong near-bottom currents (González *et al.,* 2012). The nodules grow rapidly (102–124 mm/Ma) and are characterized by a high Fe-Mn fractionation.

Fe-rich nodules from the Gulf of Cadiz are formed essentially under the influence of diagenesis, although some of the fluids in the pore water can have a deep hydrothermal origin linked to the presence of mud volcanoes. These nodules were found a depth between 500 and 1000 m covering areas of the Cadiz-contourite channel forming big nodules fields (González, 2008; González *et al.,* 2007; 2008; 2009). Recovered nodules have a rounded to discoidal shape, in section they show the presence of concentric brown to reddish coloured laminae around a nucleus formed by different type of rock or fragmented nodules. Their mineralogy is essentially formed by low crystalline goethite and lepido-

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crocite as main minerals with less amounts of birnessite and jianshuiite, (González, 2008). The geochemistry is dominated by Fe (between 14 and 45 wt% and an average of 38 wt%) and less Mn (between 3 and 9 wt% and an average of 6 %). Strategic trace elements like Co, Ni and Cu show very low contents (between 0.01 and 0.09 wt%) together with some other CRMs as Sc, Mo and REYs, due essentially to their genetic process and the fast growth rate. Interesting contents can be observed for V, Ba, Zn, (respectively 320, 340 and 62 µg/g). Shale standard (NASC) normalised patterns of REYs also confirm their diagenetic growth with negative or no Ce anomaly (González, 2008).

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