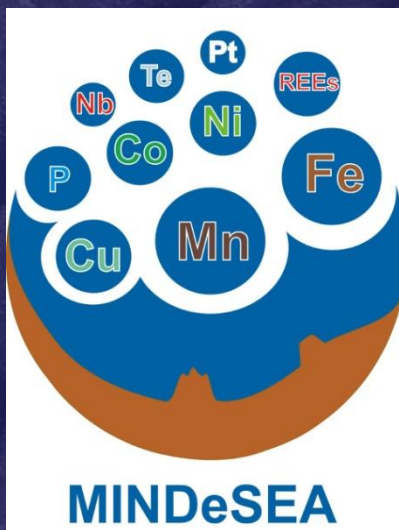


MINDeSEA

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



Deliverable 4.4: Models of formation for the main provinces of ferromanganese crusts and phosphorites

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D.4.4. models of formation for the main provinces of ferromanganese crusts and phosphorites

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 N° 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 reports the research and compilations produced by the MINDeSEA partners, led by the Geological Survey of Spain (IGME-Spain), developing the mapping and metallogenic models of marine ferromanganese crusts, phosphorites and their associated strategic and critical raw materials across all European seas. We present a general overview of the main metallogenetic areas and provinces in European seas for ferromanganese crust and phosphorites, and detailed description and maps for these seabed deposits and their associated critical elements (cobalt, phosphorous, phosphate, rare earth elements, scandium, lithium, antimony, vanadium, titanium, platinum group metals, tungsten, niobium and hafnium) in addition to strategic metals (manganese, iron, nickel, copper). A compilation map including on-land and seabed Co and P was prepared in cooperation with FRAME project (WP3). The digital version on the metallogenetic areas have been prepared, delivered with this report and will be made available through the EGD information platform (<http://www.europe-geology.eu/>).



Cross section of a cobalt-rich Fe-Mn crust from the Canary Islands. Photo: IGME.

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1. INTRODUCTION

1.1 Presentation and objectives

The MINDeSEA proposal is to compile fragmented marine data products and metadata on areas explored and investigated for ferromanganese crusts and phosphorites and make them available through the EGDI information platform (<http://www.europe-geology.eu/>). The portal will provide access to data and metadata held by each organisation based on standards developed in the Geo-Seas and EMODnet-Geology project and data products compiled at a scale of 1:250,000.

This WP will establish the location, extension and formation processes of individual European ferromanganese crust and phosphorite occurrences; how critical metals are concentrated in the mineral deposits; where they occur and why they are associated with particular minerals. This is a necessary study, to identify areas with potential Critical Raw Material (CRM) deposits as sources of strategic and critical materials within the EU and associated countries waters.

In this report we present a general overview of the main metallogenic areas and provinces in European seas for ferromanganese crust and phosphorites, and detailed description and maps for these seabed deposits and their associated critical elements (cobalt, phosphorous, phosphate, rare earth elements, scandium, lithium, antimony, vanadium, titanium, platinum group metals, tungsten, niobium and hafnium) in addition to strategic metals (manganese, iron, nickel, copper). A compilation map including on-land and seabed Co and P was prepared in cooperation with FRAME project (WP3). The digital version on the metallogenic areas have been prepared and delivered with this report. Prospectivity and mineral-potential maps, highlighting the endowment and exploration potential for selected CRM associated with submarine ferromanganese crusts and phosphorites in Europe, will be presented in the reports **D4.3** and **D4.5**.

The specific objectives of this document “Deliverable 4.4 – Models of formation for the main provinces of ferromanganese crusts and phosphorites” are the following:

- Characterize the deposit type (ferromanganese crusts and phosphorites) by compiling relevant data on the classification, geological setting, terrain, age, mineralogical and chemical composition, morphology, textural features, and other controlling parameters.
- Characterize the trace element content of the deposit type including Critical Raw Materials (CRM) for base, noble and technological metals. Study factors controlling the occurrence of the CRM.
- Identify the principal metallogenic areas and provinces where such deposits occur, taking into account spatial and temporal attributes, and provide models of formation.



1.2 General overview of submarine minerals

Covering more than 70% of the planet, oceans represent a potentially promising new frontier for the exploration of mineral resources. Security of mineral supply has been identified by the European Commission as a priority challenge facing the raw materials sector. The 2020 list of Critical Raw Materials (CRM) now reflects societies growing demand for an ever-increasing number and quantity of elements and minerals that supply the green energy and technology sectors (European Commission, 2021). The global demand for cobalt, phosphorous, rare earth elements, tellurium, nickel, lithium, copper, and other rare and critical metals, concurrent with the rapidly diminishing quality and quantity of land-based mined deposits, has situated the seafloor as a promising new frontier for the exploration of mineral resources. Studies dedicated to understanding the genesis, distribution, and resource potential of deep-sea minerals began in the late 1970s to early 1980s (Hein et al., 2013). Spanning a large diversity of environments and resource style, including high and low temperature hydrothermal deposits (seafloor massive sulphides-SMS, sedimentary exhalative deposits-SEDEX), phosphorites, cobalt-rich ferromanganese crusts, manganese nodules and rare earth elements-rich muds, deep-sea deposits are particularly attractive for their polymetallic nature with high contents of transition, rare and critical elements. Moreover, shallow-water resources, like marine placer deposits, represent another source for many critical metals and gems. The seabed mineral resources host the largest reserves on Earth for some important metals like cobalt, nickel, tellurium, manganese, vanadium, molybdenum, and others and are critical for Industry.

1.3 From exploration to mining the seabed mineral deposits

The first deep-sea discoveries comprised: 1) extensive polymetallic nodule fields in the Clarion–Clipperton Zone (CCZ) (Mero, 1962); 2) hydrothermal systems and associated metalliferous sediments, sulfide chimneys and mounds in the Red Sea and Pacific Ocean (Bäcker and Schoell, 1972; Corliss et al., 1979; MacDonald et al., 1980); and 3) Fe-Mn crusts rich in cobalt on seamounts from the Atlantic and Pacific Oceans (Halbach et al., 1982). These findings formed the bases for the research and exploratory works during the last five decades. Recent discoveries of white smokers associated with ultra-mafic hosted serpentinization (Lost City; Kelley et al., 2001) and rare earth elements-rich muds from the Pacific Ocean (Kato et al., 2011) have increased our knowledge on the diversity of mineralization styles, and the complex interactions between geosphere, biosphere and hydrosphere to form this wide variety of mineral deposits. Among the deep-sea deposits, the most interesting for their cobalt and phosphorous concentrations are ferromanganese crusts and phosphorites respectively, with a smaller impact from polymetallic nodules (Hein et al., 1997; Hein et al., 2016).

Mining of nodules anticipated to begin in the late 1970s to early 1980s did not take place. The abrupt fall in the price of base metals in the beginning of 1980s caused many of the onshore mining operations to cease, and the interest in the exploitation of marine minerals decreased. In the beginning, the commercial interest was based on base and noble metals (e.g., Mn, Cu, Zn, Au, Ag).



Rare metals (e.g., Co, Te, Nb, Pt) and REE beneficiation as by-products of mining of the major metals have centered the research undertaken in the last decade (Hein et al., 2013). Actually, vast areas of deep-ocean floor have been contracted for exploration, and more contracts are taken out every year. The International Seabed Authority (ISA) is finishing the exploitation regulations that will permit State parties, State enterprises or natural or juridical persons or consortia of entities to extract minerals in areas beyond national jurisdictions, the so-called “Area”. In 2000, 2010 and 2012, the Council and Assembly of the ISA passed regulations for the exploration for polymetallic nodules, polymetallic sulfides, and cobalt-rich ferromanganese crusts respectively (ISA, 2021). Thirty contractors have entered into 15-year contracts with ISA for exploration for polymetallic nodules, polymetallic sulphides, and cobalt-rich ferromanganese crusts on the deep seabed of the Atlantic, Pacific, and Indian oceans (ISA, 2021). Over the 15 years, these exploration areas will be subject of relinquishment and will be smaller by the end of the contract (not more than 2500 km² in the case of polymetallic sulphides and not more than 1000 km² in the case of cobalt-rich ferromanganese crusts). Now, various deep-ocean small mines are scheduled to start operations in the Red Sea, Southeast Atlantic and Southwest Pacific Ocean within the next years within national jurisdictions (Fig. 1).

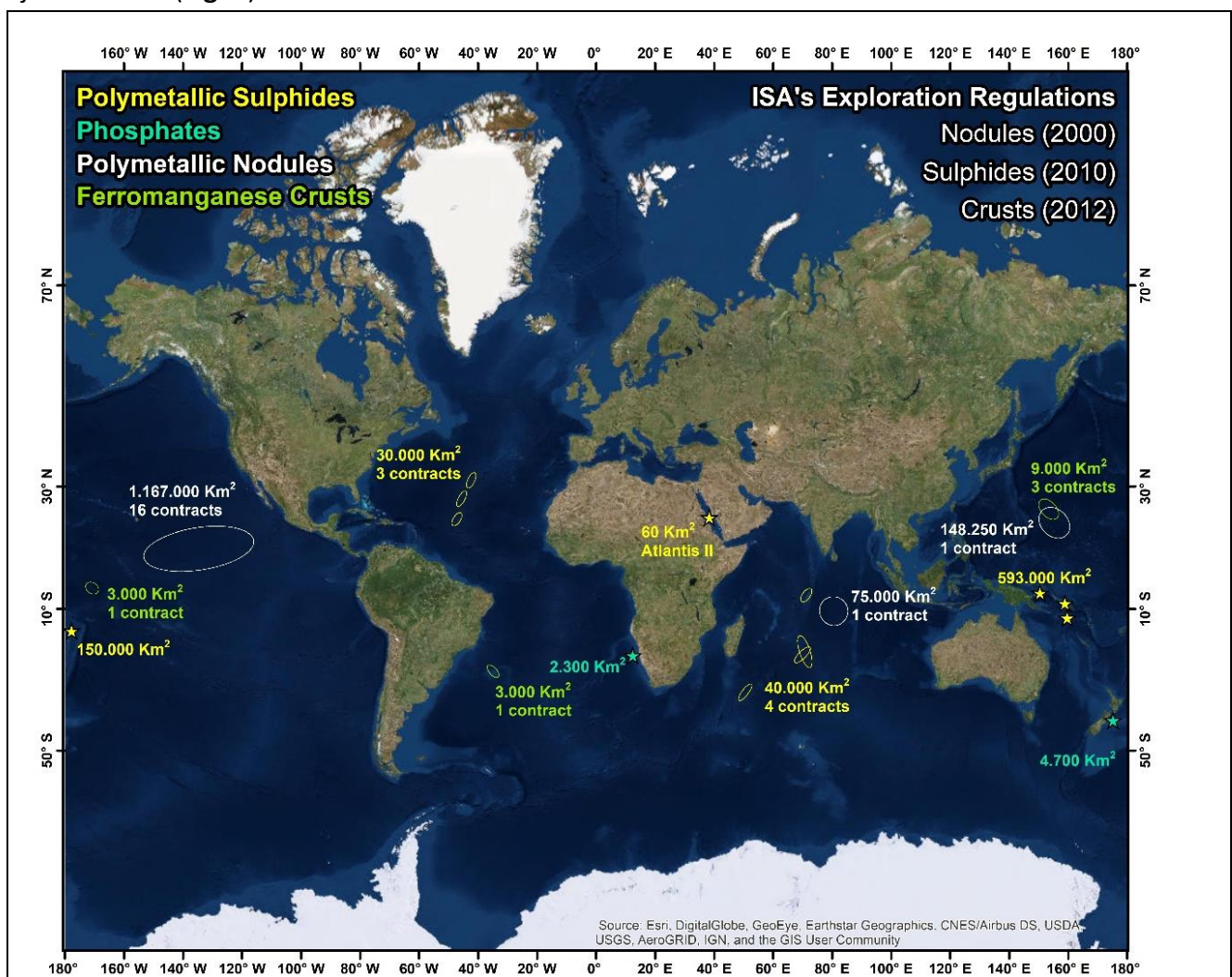


Figure 1. Global map of seabed minerals exploration present status. The stars represent areas under national jurisdictions. Modified from Hein et al. (2013).

1.4 Ferromanganese crust and phosphorites

Marine ferromanganese crust deposits are potential mineral resources that contain base metals and strategic and critical elements such as copper (Cu), cobalt (Co), vanadium (V), nickel (Ni), titanium (Ti), platinum group metals (PGM) or rare earth elements (REE). Traditionally, marine precipitates are defined as: a) purely hydrogenetic when all constituents are derived from cold seawater, (b) diagenetic, when all constituents are derived from cold sediment pore water; and (c) hydrothermal when precipitation occurs in the vicinity of hydrothermal vent sites from fluids with temperatures higher than ambient bottom waters. Hydrogenetic Fe-Mn crusts occur throughout the global ocean on seamounts, ridges and plateaus, where currents have kept the rocks free of sediment for millions of years. Some ferromanganese (Fe-Mn) crusts exhibit a mixed origin, primarily either hydrothermal-hydrogenetic or hydrogenetic-diagenetic (Hein et al., 2000; 2003; 2013; Muiños et al. 2013; Bau et al., 2014; Marino et al., 2017).

In many places, marine phosphorites are accompanied by Fe-Mn crust deposits on the seafloor of continental shelves and slopes along the western continental margins of the Atlantic Ocean. Some thick Fe-Mn crusts also contain carbonate fluorapatite, which was incorporated into the crusts during specific periods prior to the middle Miocene during main Cenozoic episodes of phosphatization. These deposits are related to strong upwelling along the continental margins and seamounts. Marine phosphorites are known to concentrate REE and yttrium (REY) during early diagenetic formation (Hein et al., 1993; 2016; González et al., 2016). Although there are several references to ferromanganese crusts and their association with phosphorites in the literature, the genetic models for explaining their relationship and metal concentration are still poorly understood.

Research on phosphorites and Fe-Mn deposits have traditionally had two main purposes: 1) their economic importance as potential sources of phosphate for agriculture, and metals, REY, among others, required for high-tech and green-tech applications; and 2) their potential as archives for the study of paleoceanographic events.

Phosphorite and ferromanganese crust deposits are frequently associated, and widespread on the seafloor of continental shelves and slopes along the western continental margins of the Atlantic Ocean, also occurring on seamounts, banks and plateaus. They are especially abundant on the volcanic seamounts and ridges from the Macaronesia region (Canary-Madeira-Açores Islands) and the Atlantic Iberian margins.

2. SEABED MORPHO-TECTONIC ENVIRONMENTS

2.1 Evolution of the Atlantic and European marine basins

The oceans display several different morphotectonic units, each having its own morphology and history. Their formation is related to the evolution of the different oceans and to the tectonic processes that take place between continental and oceanic plates (Kotliński, 1999).



The oceans undergo continuous evolution, where palaeoceanographic reconstructions show that they have changed, shape, aerial extent, and depth through the history of the Earth. Marine morpho-tectonic structures formed by different processes during the formation of the oceans. In Europe, marine environments are represented essentially by the Atlantic and Arctic oceans together with the Mediterranean, Black, North, Baltic, Kara and Barents seas. The Atlantic Ocean started opening around 200 Ma ago when the Pangea supercontinent started to rift in the Early Mesozoic. The opening of the Atlantic Ocean can be divided in two main phases, the first one during the Early-Middle Jurassic with the separation of North America and Africa and the second in the Early Cretaceous when Africa separated from South America (Seton et al., 2012). The first rifting episode of Pangea also contributed to the formation of the Arctic Ocean as the rift moved northward during the Triassic, and later during the Cretaceous the Canadian Basin started to open with the separation of the North America and Eurasia, and finally the Amerasia Basin opened during the Late Cretaceous with spreading through the Alpha-Mendeleev Ridge (Gaina et al., 2014; Nikishin et al., 2017).

The North Sea first formed during the rifting of the supercontinent Pangea (200 Ma), and its evolution continued during the Jurassic and Cretaceous with different extensional tectonics, but is in the Cenozoic the North Sea reached its current morphology due to thermal subsidence caused by the rifting that started in the Late Cretaceous (Graversen, 2006). The origin and formation of the Baltic Sea is still under discussion, with some researches considering that the basin formed during the Cenozoic (Voipio, 1981) while others think that the basin is the result of erosion from a complex system of rivers and lakes during the Cenozoic (Bijlsma, 1981; Marks, 2004). During Quaternary glaciations the depression of the Baltic Sea was covered by ice sheets that brought sediments from the adjacent areas that caused subsidence and isostatic rebound after retreat (Andrén et al., 2011).

The Barents and Kara marginal seas formed after the opening of the Arctic Ocean. The Barents Sea formed during extensional tectonic episodes that occurred after the Caledonian orogeny and the collision of Laurasia with Western Siberia. The Kara Sea, on the other hand, lies on the Siberian Shelf and was formed as a result of deglaciation during the last Ice Age (Svendsen et al., 2004).

The Mediterranean Sea history is quite complex, part of it is the remnant of the Tethys Ocean located between Gondwana and Laurasia during the Mesozoic. Due to the convergence of the African and Eurasian plates it started to close between the Late Triassic and the Jurassic when Cimmeria collided with Laurasia creating a landlocked body of water. Due to this and to the dry climate, it started to evaporate but it was during the Messinian when the Mediterranean Sea became landlocked causing great amounts of evaporites to form. Finally, 5.3 million years ago, the Mediterranean Sea reopened and was refilled in less than two years by the Zanclean flood; the current flow in the Strait of Gibraltar is three orders of magnitude higher than the Amazon River flow. The Black Sea formation is also related to the closure of the Tethys Ocean and the result of back-arc extension associated to the subduction of the Tethys in the north during the Mesozoic (Robinson et al., 1996). During collision of the African and Eurasian plates (Late Triassic and Jurassic) and the formation of the North Anatolian and East Anatolian Fault systems initiation of subsidence



began and volcanic activity ensued. The offset of the western and eastern Black Sea basins, separated by the mid-Black Sea Ridge, originated along a former Albian volcanic arc during the Cenomanian and Coniacian (Nikishin, 2003).

2.2 Marine geo-tectonic settings

Fe-Mn crust mineralization is generally associated with the presence of hard substrates on which Fe and Mn oxyhydroxide colloids can accumulate during millions of years (Bogdanov et al., 1990; 1995; Hein et al., 1997; 2000; Bogdanova et al., 2008; Marino 2020). These hard substrates are represented by positive relief that rises from abyssal depths forming different morpho-tectonic structures suitable for the accretion of the Fe-Mn crusts or suitable for the accumulation of phosphates linked to upwelling and bioproductivity. The origin of the different oceans and seas together with the presence of intraplate volcanism and tectonic activity resulted in the formation of all the morpho-tectonic environments in which Fe-Mn crusts or phosphates accumulated through time. Among them, the most important are represented by the continental shelf of shallow seas, seamounts, banks and plateaus, and ridges that can be found in almost all the oceans and seas surrounding Europe.

2.2.1 Shallow seas

The shallow seas developed on the broad continental shelf that is the natural prolongation of the continents and represent the transition between land and deep oceans. In marine science, a “shelf” is a shallow underwater extension of a land, either a continent “continental shelf” or large island “island shelf” (Hay, 2016). The actual geomorphology in the shallow seas is the result of different factors and relict structures during their evolution. The most important factors are glacio-eustatic and tectonic changes in sea-level and also sedimentary processes acting (Fig. 2) (Durán and Guillén, 2018). These changes act at scales of millions of years and control the morphology of the continental shelf and consequently the supply of sediments and their composition but also the movement of currents. The main landforms that is possible to find in shallow seas are grouped as: (a) associated to consolidated bottoms, (b) erosive morphologies, (c) prograding landforms, (d) bedforms, (e) gas-related features, and (f) anthropogenic features (Durán and Guillén, 2018).



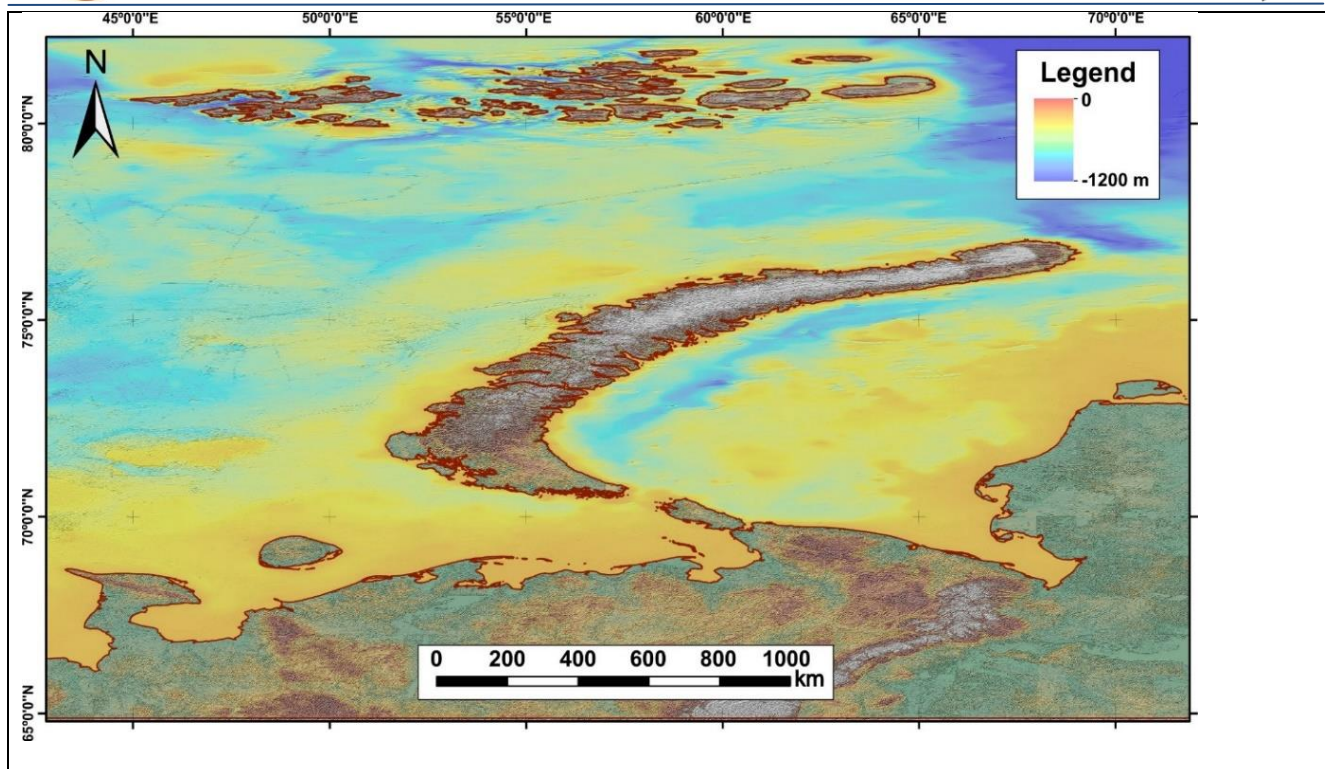


Figure 2. Bathymetric model of Barents Sea, a shallow water area in the Arctic Ocean region.

2.2.2 Seamounts

Seamounts are defined as any geographically isolated submarine features taller than 100 m not located on the continental shelves (Staudigel and Clague, 2010). Also, the term guyot can be used as a synonym representing a seamount with a truncated cone shape usually with a flat summit produced by erosion at sea-level, formation of carbonate reef, or caldera collapse (Buchs et al., 2016). Most of the seamounts formed by volcanism and other igneous activity in different areas, such as close the mid-ocean ridges, on-axis if they are on the mid-ridge or off-axis if they are farther away but on relatively young crust, islands arcs, and intraplate settings (Buchs et al., 2016); in places, blocks of continental crust fragmented during the opening of the oceans can form non-volcanic seamounts (Mortimer et al., 2006). Intra-plate seamount provinces are formed near spreading centers along relatively young crust or, typically they formed by at “hot spots” where mantle plumes breach old oceanic crust (i.e. Canary Islands seamount province or Madeira province) (Geldemacher, 2008; Buchs et al., 2016).

Volcanic seamounts are formed by eruptive and intrusive products. Eruptive products are represented essentially by pillow lavas, at medium and slow effusive rates, and in massive sheets at high effusive rates while intrusive products are represented by dikes, sills, and plutonic rocks varying from gabbros to ultramafic (Buchs et al., 2016). The growth of a volcanic seamount is due by the alternation of effusive and intrusive magmatism, also explosive eruptions can occur when the magma interacts rapidly with the water or when the magma has high contents of volatiles that rapidly degas under low-pressure conditions (shallow water) (Fig. 3).

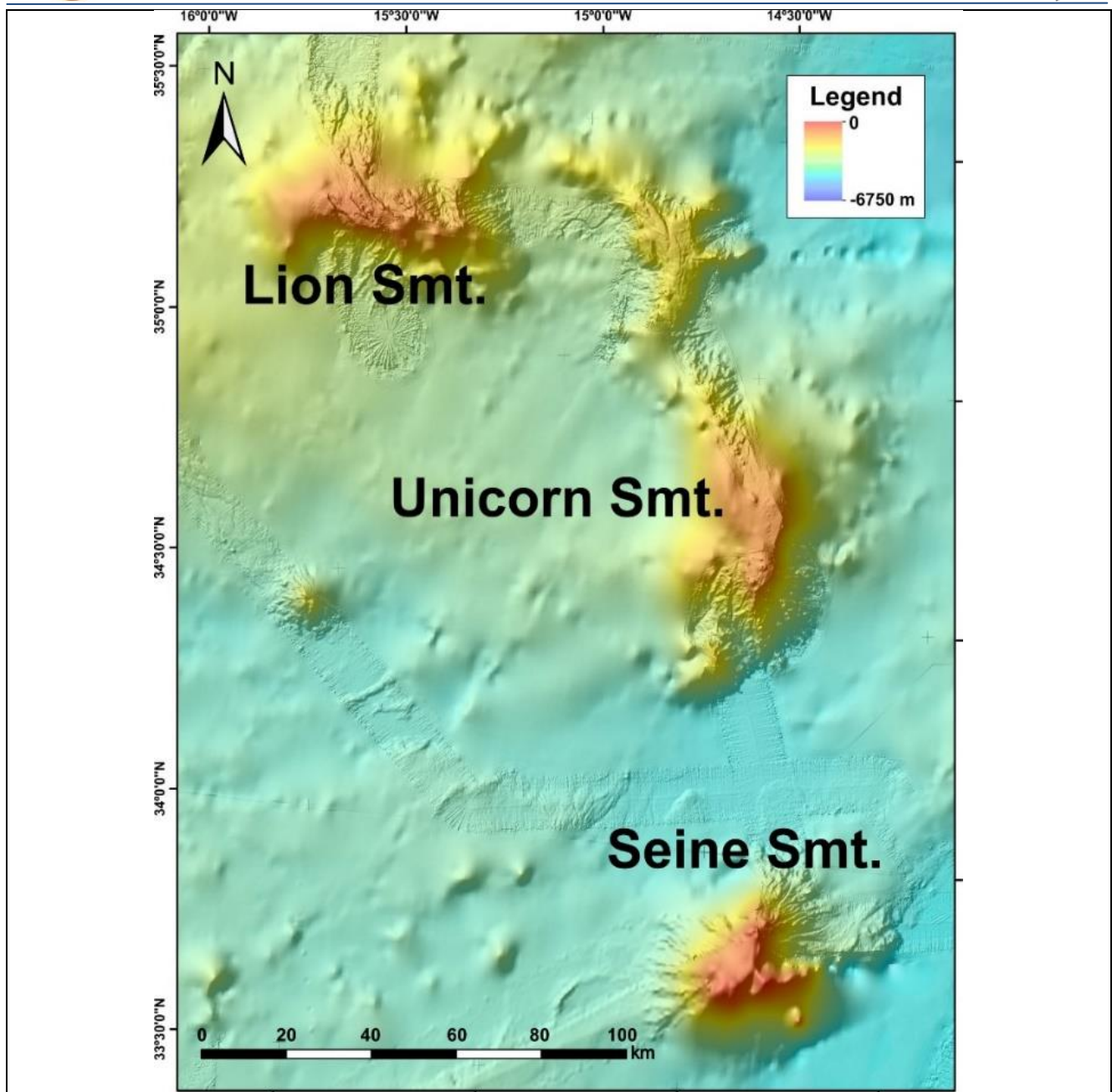


Figure 3. Bathymetric model of seamounts in the region of Macaronesia (Atlantic Ocean).

The formation of a seamount can be subdivided in six phases (Staudigel and Clague, 2010):

- Formation of a small seamount during incipient volcanism after a magmatic interaction with marine sediments, in most, the magma supply rapidly vanishes and the seamount remains small.
- Rarely, the seamount shows continued volcanic activity that finally results in the formation of a much larger volcano.
- When the summit of the seamount is near the sea-level, explosive volcanism is higher. In this case, clastic deposits form on the slopes and some seamounts emerge forming an island when the eruption rate is faster than the erosion rate.

- Being subaerial with continue volcanism, the seamounts can develop carbonate reefs along the shoreline.
- When volcanism stops, the island starts to erode. During this stage, the collapse of slopes (sector collapse) can remove large parts of the volcanic edifice with the possibility of tsunami formation. During this step, the volcanism can stop for millions of years and then reactivate during a volcanic rejuvenation period. The erosion leads to the formation of a flat top during subsidence through lithospheric cooling and glacio-eustatic changes, which can lead to the formation of a “guyot” and submerge the volcano to more than a 1000 m (i.e. Echo and Tropic seamounts in Canary Islands).
- Most seamounts along active margins are finally transported to subduction zones and the formation of faults can lead to the partial collapse, segmentation, or decapitation of the edifice. Also, during the subduction, the seamount and related products can accumulate in the accretionary wedge (Buch^s et al., 2016).

2.2.3 Banks and plateaus

Marine banks and plateaus form large elevated areas in the oceans that are bigger than guyots and can occur in the oceans both as part of submerged continental crust or as thick oceanic crust.

Banks and plateaus of continental crust can form as relict continental crust separated by faults from the continents during the opening of the oceans and can be found near the continental margin (i.e. Galicia Bank and Rockall Plateaus) (Roberts, 1975) (Figs. 4 and 5). On the other hand, oceanic plateaus are formed by decompression melting of hot mantle plumes (Kerr, 2016). Due to the vast volumes of erupted or intruded magmas they are classified as large igneous provinces (LIP). LIP are defined as areas with an extent $>0.1 \times 10^6 \text{ km}^2$ and an igneous volume $>0.1 \times 10^6 \text{ km}^3$ during a time of almost 50 Ma, with intraplate tectonic and geochemical affinities that are characterized by short igneous pulses (1-5 Ma) in which most of the total igneous volume ($>75\%$) is emplaced (Kerr, 2016). These plateaus were discovered in the early 1970s from seismic surveys that revealed several portions of the ocean with thicker crust (6-7 km) but the term “oceanic plateau” was used for the first time by Kroenke (1974) to describe a large area of thickened crust ($>30 \text{ km}$) now known as Ontong Java Plateau in the West Pacific. In European Seas, the Oceanic plateaus are represented essentially by the North Atlantic Igneous Province (NAIP) (Kerr, 2016), which includes the Iceland Plateau and the Azores Plateau both formed by the continuous magmatism from the Mid Atlantic Ridge (Fig. 4).



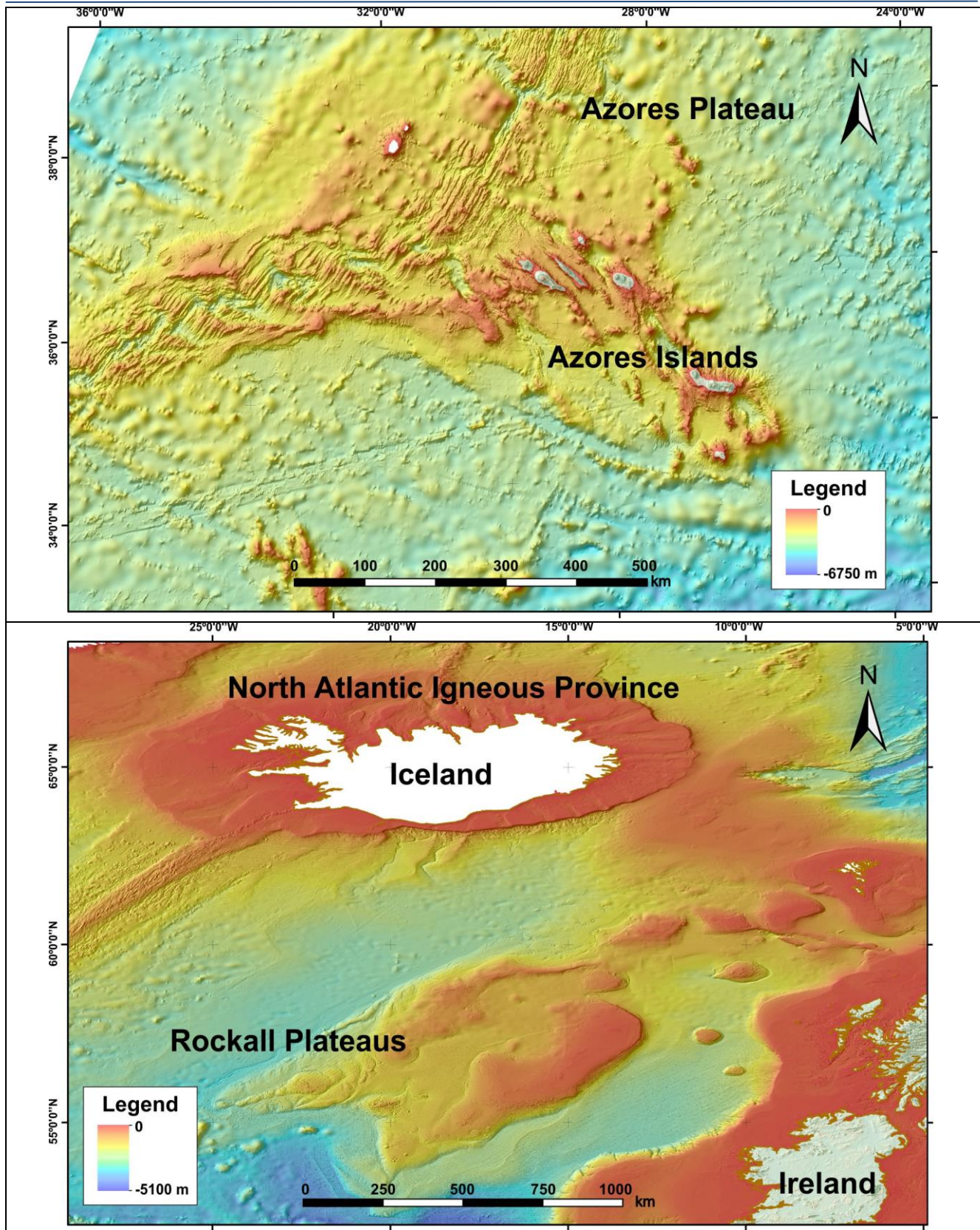


Figure 4. Bathymetric models of the Azores Plateau in the Macaronesia and the Rockall Plateaus (NE Atlantic Ocean).

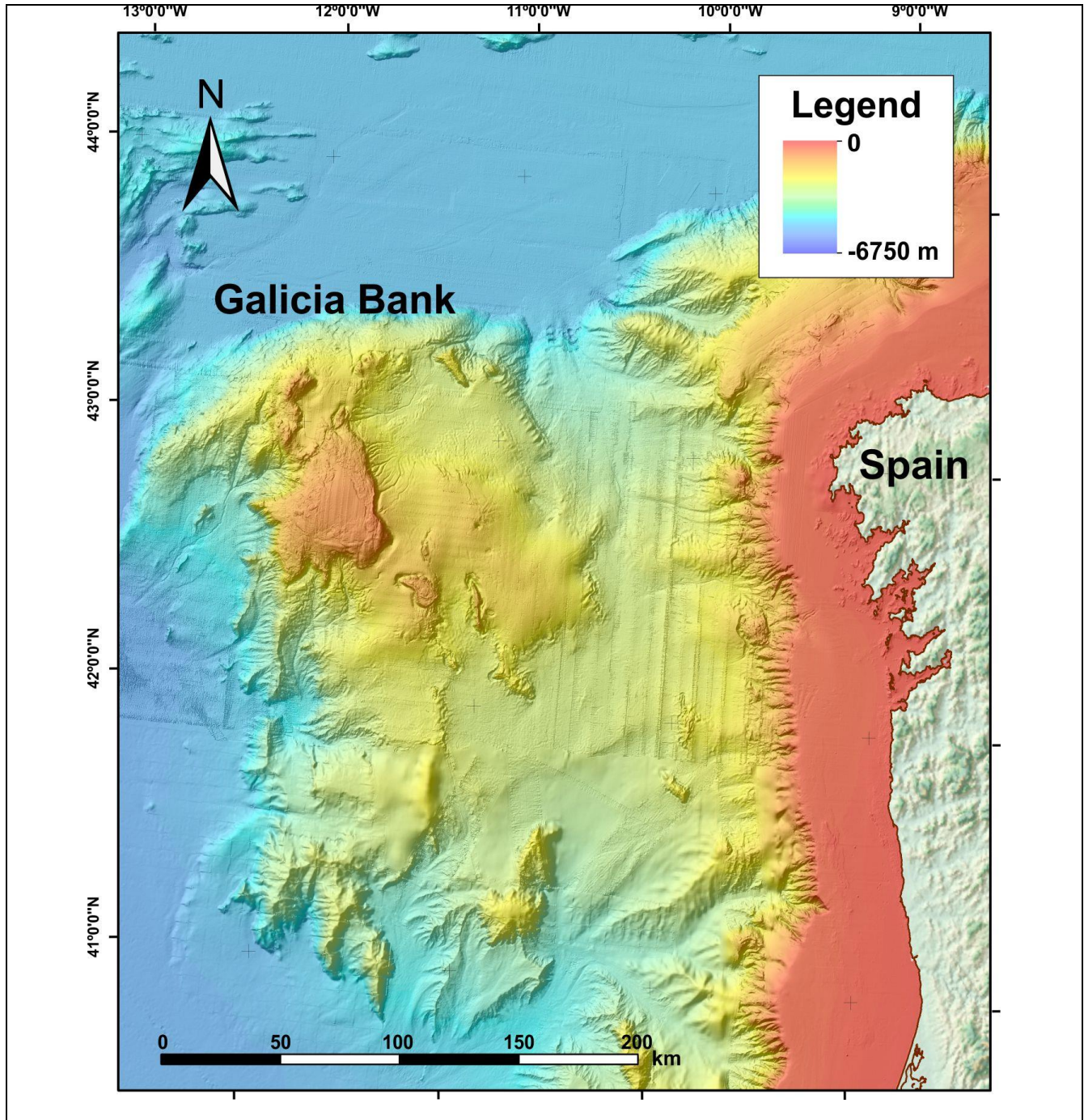


Figure 5. Bathymetric model of the Galicia Bank region in the Atlantic Iberian margins.

2.2.4 Ridges

Mid-Ocean Ridges (MOR) are linear volcanic and tectonic regions marking the constructive boundary between two tectonic plates (Rubin, 2016). These ridges can be found in all the oceans, in places emergent as seen in Iceland. MOR morphology is a direct consequence of the rate of magma extrusion, the newly formed oceanic crust possessing a lower density with respect to much older crust due to its internal heat. The main morphology is represented by linear volcanic elevations divided in segments by transform faults, the inclination of the slopes depends on the evolution of the ridge and the formation of oceanic crust, in areas with slow spreading the MOR has a relatively

flat morphology with gentle slopes and a central area called a “median valley”. Due to slow spreading, there is the possibility of the formation of a series of pull-apart faults parallel to the central axis, as on the North Atlantic Ridge (Ewing et al., 1953). On the other hand, fast spreading ridges show an elevated morphology with a rough crest along the axis and steep slopes, as seen in some parts of the East Pacific Rise (Rubin, 2016).

Other types of ridges forming chains of seamounts or elongation due to the magma release along elongated fractures may represent the aborted evolution of a MOR (Figs. 6 and 7).

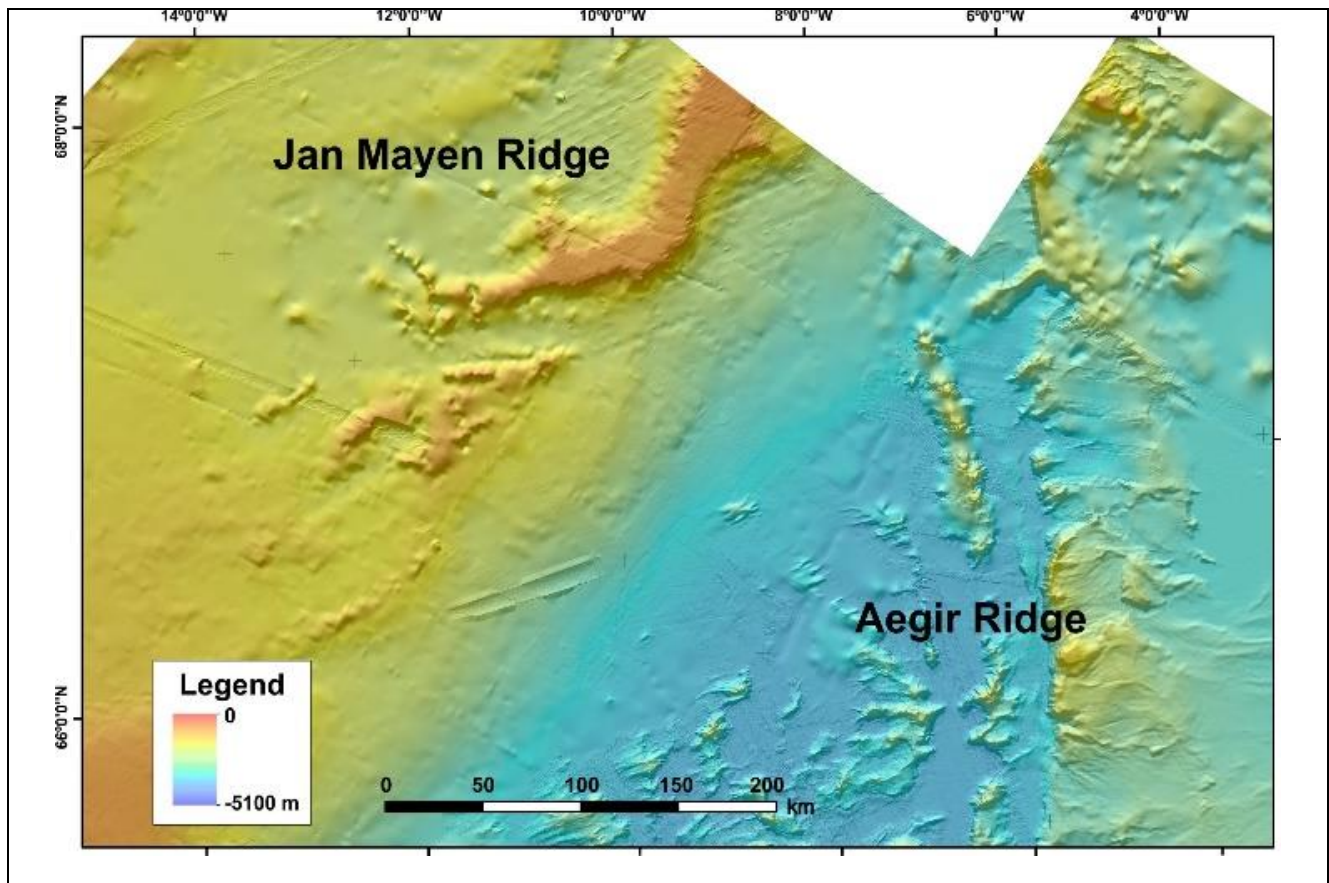


Figure 6. Bathymetric model of Jan Mayen and Aegir ridges in the Norwegian margin.

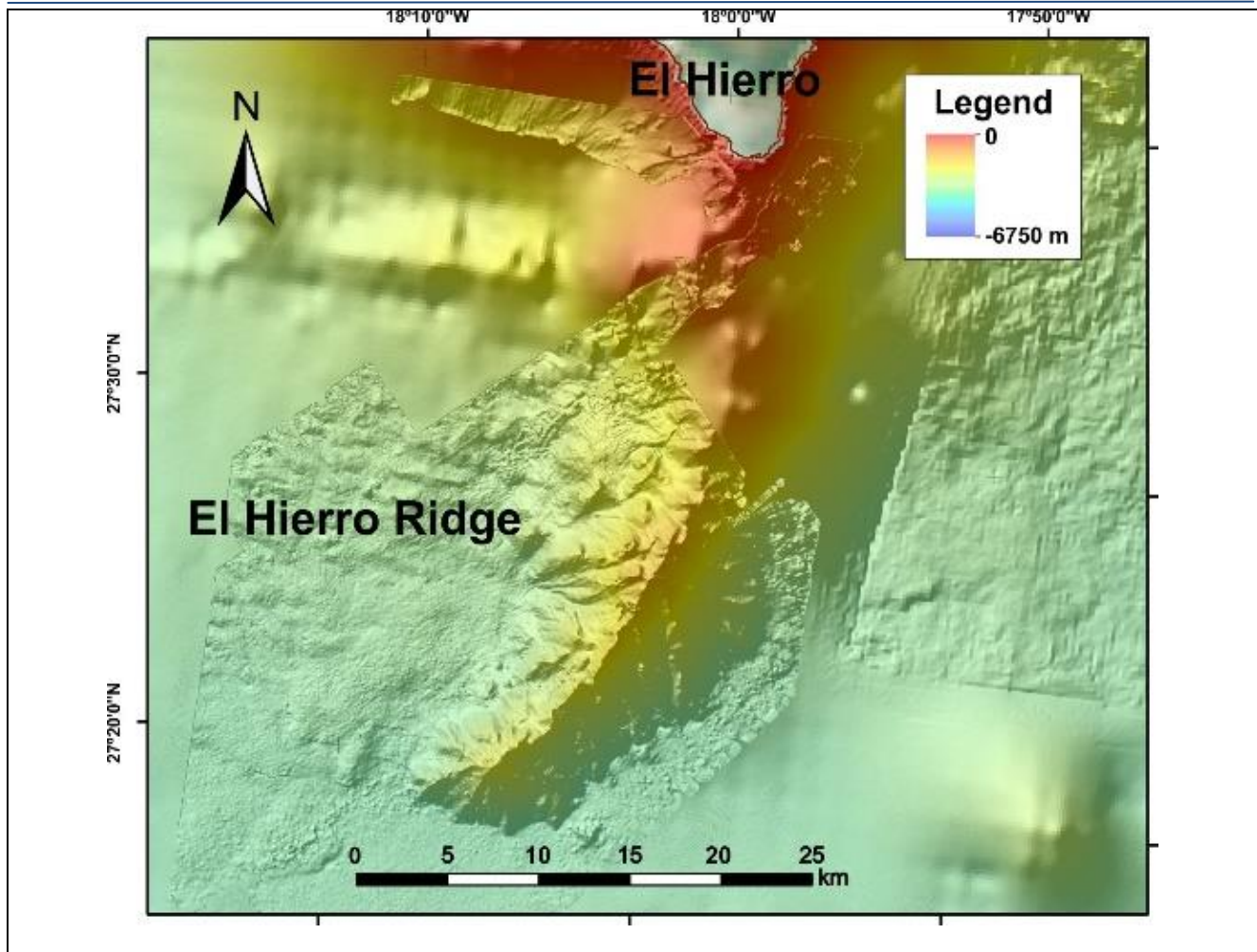


Figure 7. Bathymetric model of El Hierro Ridge in the Macaronesia region.

2.2.5 Abyssal planes

Abyssal planes are the flat areas of the seabed with depths from 3000 to 5000 m that show a gradient below 0.1° . These areas occupy over the 28% of the total seafloor with a sediment cover of up to 1000 m thickness of essentially fine-grained detritus and biogenic particles (Voelker, 2016). The name comes after the first global map of the seafloor published in 1977 in which it was possible to see that the bottom of the oceans is bordered by continents and contain several mountain chains (seamounts) and ridges (Voelker, 2016). In this map can also be seen that between these morphologies exist vast areas of flat regions that represent the abyssal planes. After this first attempt, seafloor maps have been refined many times that allow quantitative analyses of global morphological types distributions (Voelker, 2016).

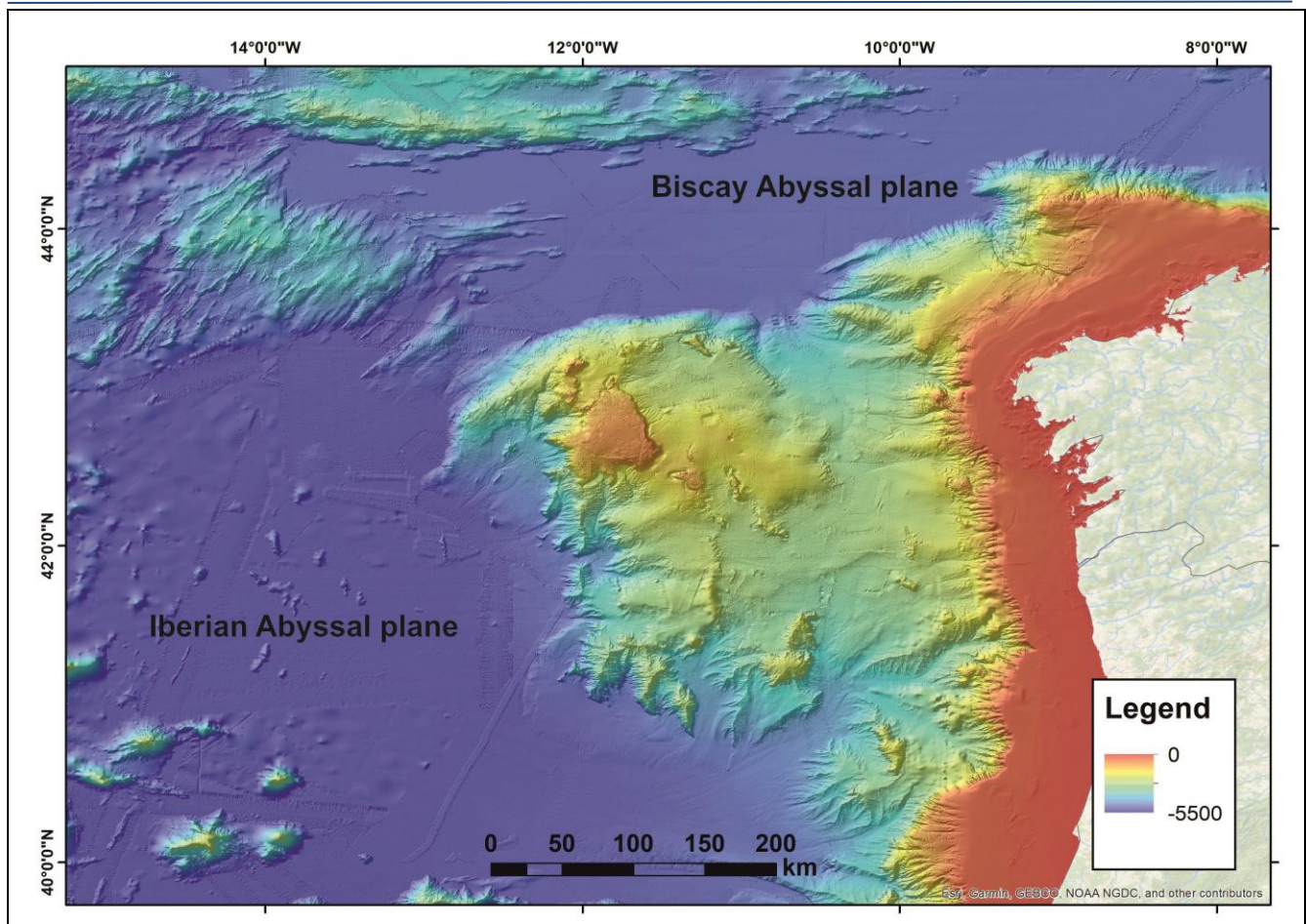


Figure 8. Bathymetric model of Biscay Abyssal Plane and Iberia Abyssal plane in the Bay of Biscay and Iberian Coast marine region

On the abyssal planes, accumulated sediments derive from continents and islands, and also sediments produced for example in the formation and dismantling of seamounts, banks, and ridges. Moreover, sediments are also represented by the accumulation of biogenic detritus. Sedimentation rates are very low, in the order of 1-5 cm/Ka while near the continental margin these rates are 100 to 1000 times higher (Voelker, 2016).

In pan-European Seas the abyssal planes can be found in the area between the Macaronesian islands (Canary Islands, Madeira, Azores) (Fig. 8) and the Iberian margin and also in the area between the north of Spain, England, and France (Voelker, 2016).

3. MARINE REGIONS AND MINDESEA DATASET

3.1 European marine regions

Marine regions localized and used in this report correspond to those adopted by the EU Marine Strategy Framework Directive (MSFD) with the aim to protect more effectively the marine environment across Europe (<https://www.eea.europa.eu/data-and-maps/data/europe-seas>) (Table 1).

Marine regions	Subregions
Baltic Sea	
North-east Atlantic Ocean	- Greater North Sea - Celtic Seas - Bay of Biscay and the Iberian Coast - Macaronesia
Mediterranean Sea	- Western Mediterranean Sea - Adriatic Sea - Ionian Sea and Central Mediterranean Sea - Aegean-Levantine Sea
Black Sea	

Table 1. The MSFD separates European seas into four main regions and eight sub-regions.

Together with these regions in the MINDeSEA project is also the Norwegian Sea, Greenland Sea, Iceland Sea, Barents Sea, and White Sea subregions that are part of the Arctic Ocean (**Fig. 9**).



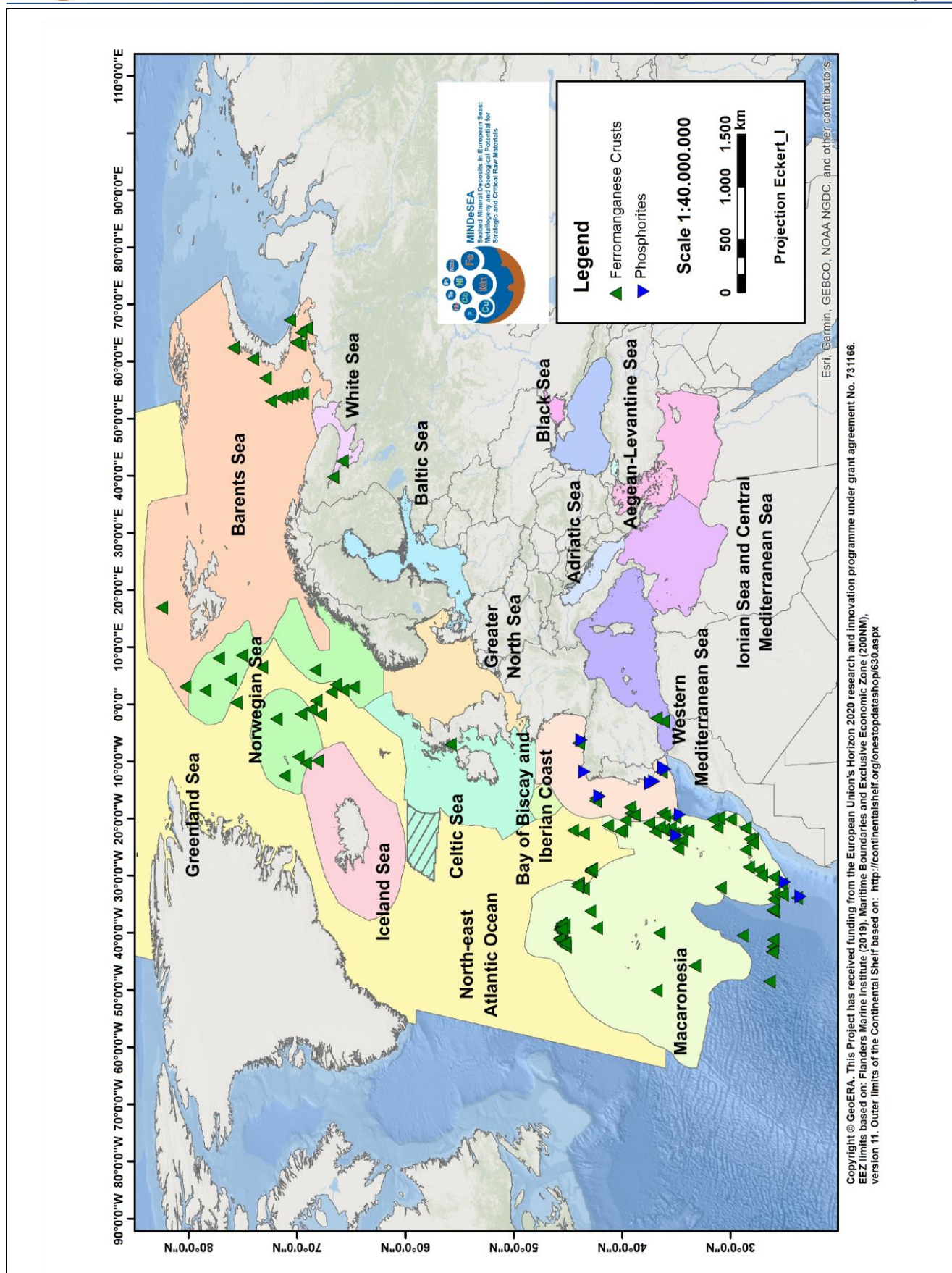


Figure 9. Spatial distribution of ferromanganese crust and phosphorite occurrences, in relation to the MSFD marine regions/sub regions, compiled in the MINDeSEA project.



43.2. Ferromanganese crusts and phosphorites – general data

In the MINDeSEA database are listed a total of 141 ferromanganese crusts occurrences. The marine region with the highest presence of Fe-Mn crusts occurrences is Macaronesia and surrounding areas out of the European jurisdictions in which are 78 of those 141 occurrences, corresponding to 55% of the total. In the Northeast Atlantic Ocean are 20 occurrences, followed by the Barents Sea with 16 occurrences, the Norwegian Sea with 11, and the Bay of Biscay and the Iberian Coast show 10 occurrences. Finally, in the White Sea and in the Western Mediterranean Sea there are 2 occurrences each and in the Celtic and Iceland seas also one occurrence each.

Phosphorites occurrences have been found only in the area of the Bay of Biscay and Iberian Coast in which are listed 8 occurrences and in the Macaronesia in which are listed 4 occurrences. All these phosphate occurrences are linked to the Spanish and Portuguese EEZ and ECS.

3.2.1 Barents and White seas

In the Barents Sea region are sixteen occurrences in the MINDeSEA database. Generally, in this area Fe-Mn crusts can be found as thin concretions enriched in Fe and found at shallow water depths (average 250 m depth) and linked to the presence of hard surfaces formed by submarine banks (**Fig. 10**).

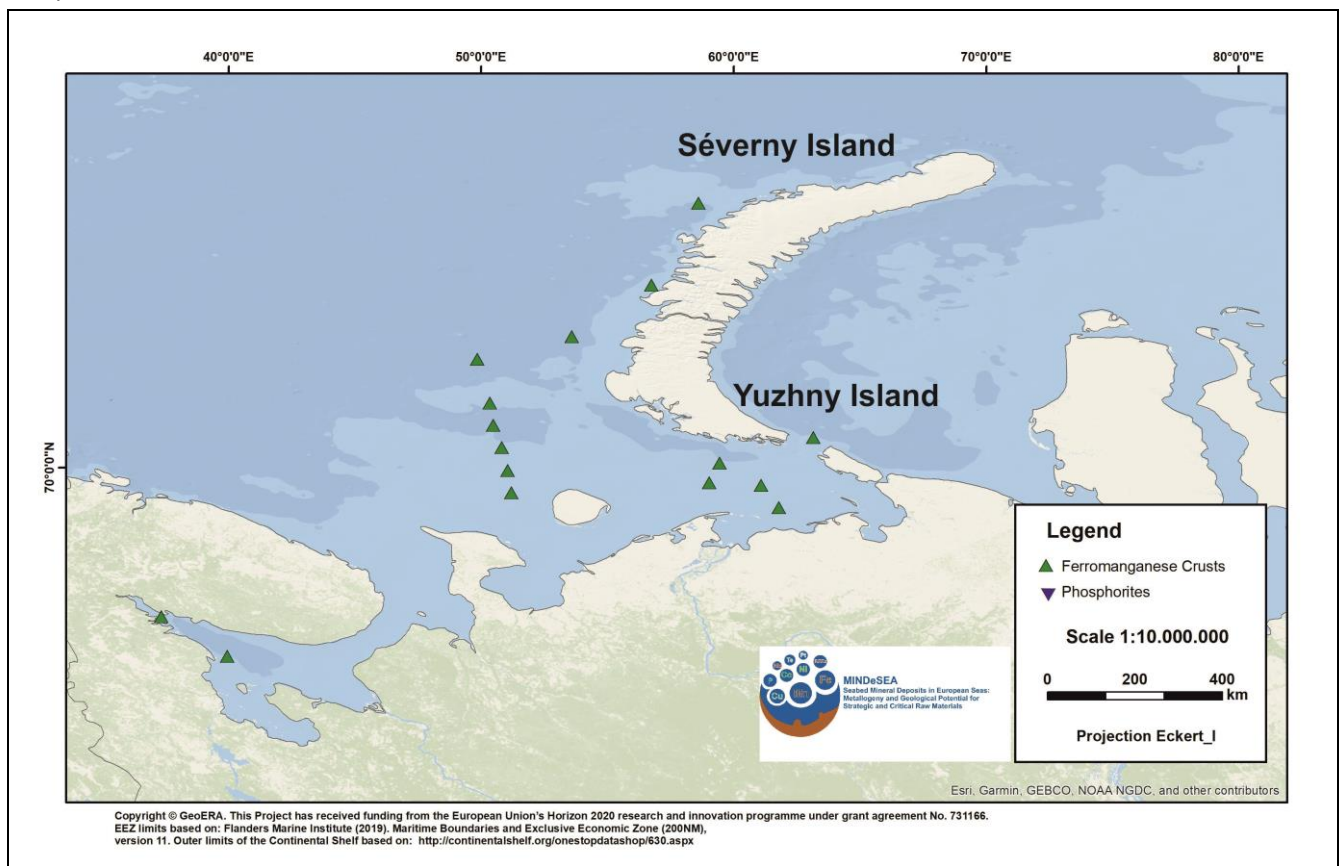


Figure 10. Location of ferromanganese crusts occurrences in the Barents and White seas.

3.2.2 Macaronesia

The MINDeSEA database shows 78 occurrences of Fe-Mn crusts in this region surrounding the Canary Islands, Madeira, and Azores archipelagos (**Fig. 11**). Twenty-one locations are within the Spanish EEZ and ECS and forty-five within the Portuguese EEZ and ECS. The rest of occurrences occur in the area of the Atlantic Ocean located just southwest of Macaronesia in the Central Atlantic Ocean. The typical marine setting for the formation of Fe-Mn crusts in this area is represented by volcanic seamounts located in base water depths 5000 and 250 m.

In this region the MINDeSEA database lists four occurrences of marine phosphorites all of them linked on seamounts. Two of these occurrences are in the Spanish EEZ and ECS while the other two are located in the Portuguese EEZ and ECS (**Fig.11**).

3.2.3 Norwegian Sea

In the Norwegian Sea the occurrences of Fe-Mn crusts can be found essentially linked to ridges and seamounts located. The ridges are essentially represented by the triple junction formed between the Mid Atlantic, Jan Mayen, and Mohns ridges (**Fig. 12**). Also, in the northern part of this region occur several submarine highs formed around the MAR.

3.2.4 Bay of Biscay and Iberian coast

In this region the occurrences of Fe-Mn crusts are located within the EEZ of Spain, Portugal, and France, associated both along the continental shelf and on seamounts and plateaus located near the coast.

In this area, we separate three main locations. The first group of three occurrences are linked to the Galicia Bank area and smaller seamounts located on the north of the Iberian Peninsula, in outbound of the Cantabrian coast. In this area, Fe-Mn crusts can be found at depths between 5000 and 500 m (**Fig. 13**). Another group of six occurrences are located along the Madeira-Tore rise and neighboring seamounts located in the Portuguese EEZ. In this area, Fe-Mn crusts can be found at depths ranging from 3000 and 500 m (**Fig. 13**). Finally, a final occurrence is found on a seamount also located in the Portuguese EEZ in the Gulf of Cadiz and at a shallow depth (460 m) compared with the other two areas (**Fig. 13**).

Phosphorites are also present with eight occurrences in this region located essentially on the Iberian continental shelf and Galicia Bank area. Four occurrences are within the Spanish EEZ and ECS limits, two occurrences in the Galicia Bank and neighboring seamount (Sancho Seamount). One occurrence is located on the Ortegal Terrace 40 km north from the Galicia coast, and finally the last occurrence is found on Le Danois Bank, 80 km from the Cantabrian coast (**Fig. 13**). The other four occurrences are located within the Portuguese EEZ, two in the Gulf of Cadiz area (on the Guadalquivir Bank and Faro Plateau) and the other two in the Alentejo Basin (on the Descobridores and Prince de Avis seamounts) (**Fig. 13**).



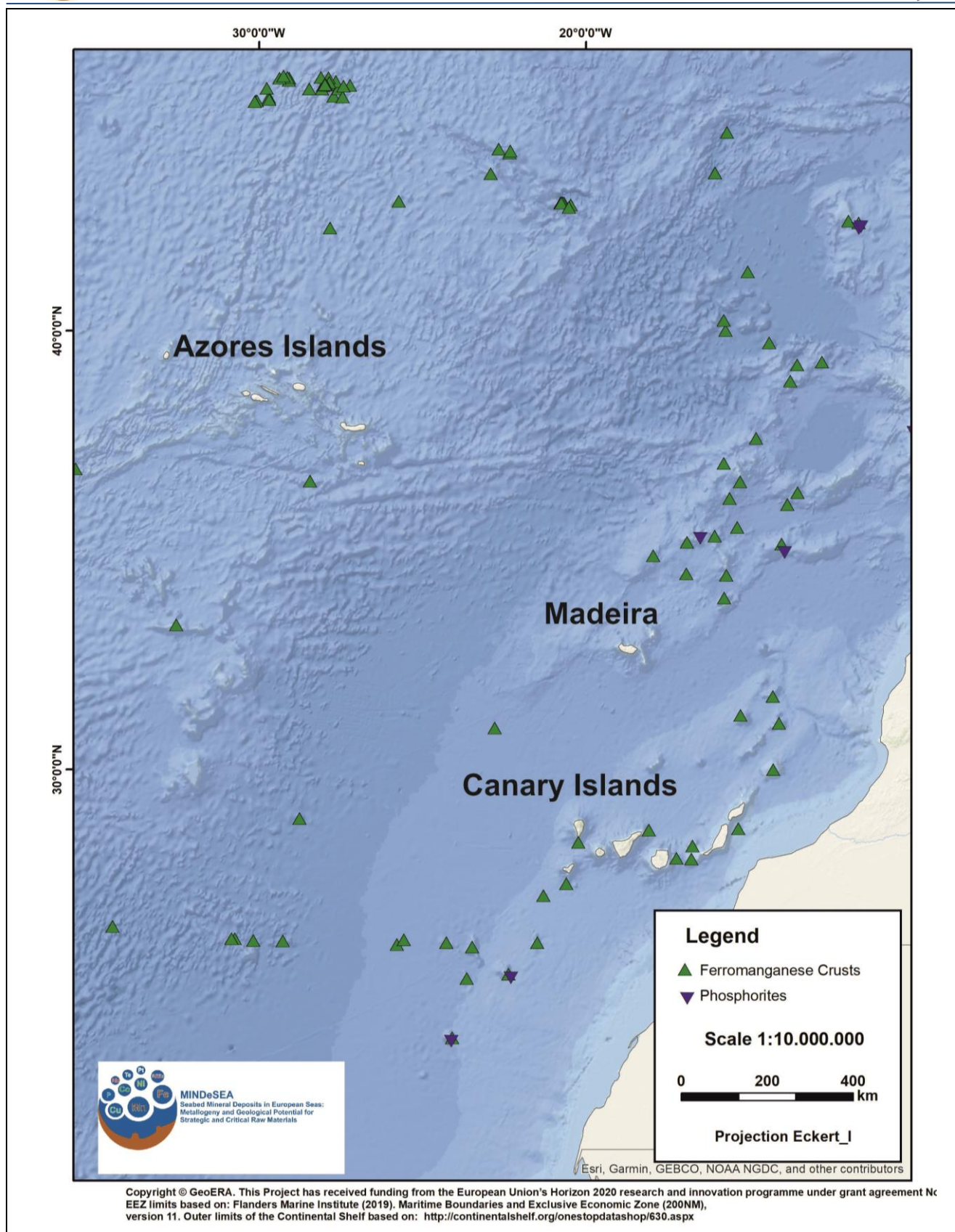


Figure 11. Location of ferromanganese crust and phosphorite occurrences rich in Co, Te and REY in the Macaronesia area.

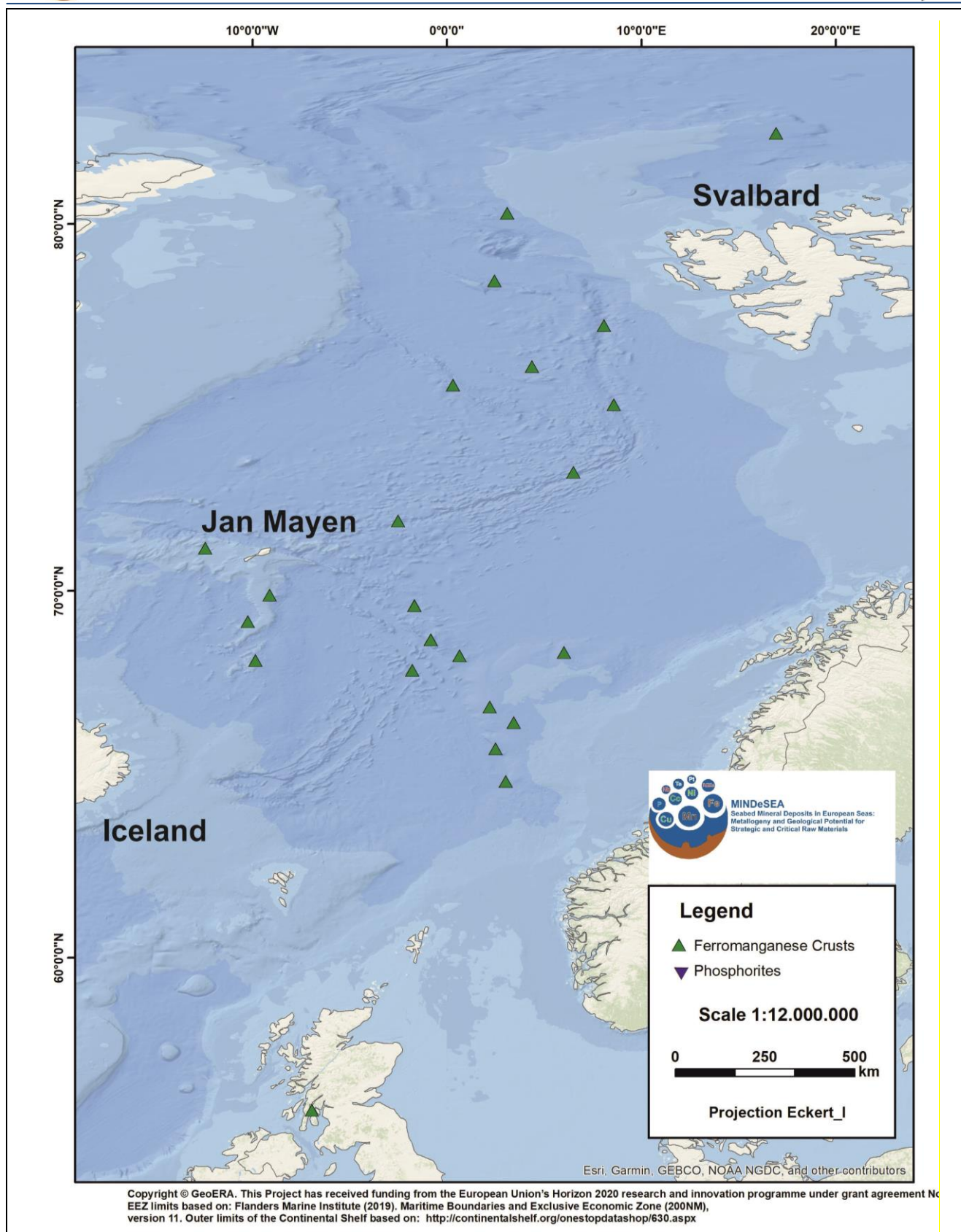


Figure 12. Location of ferromanganese crust occurrences in the Northeast Atlantic and Norwegian Sea.

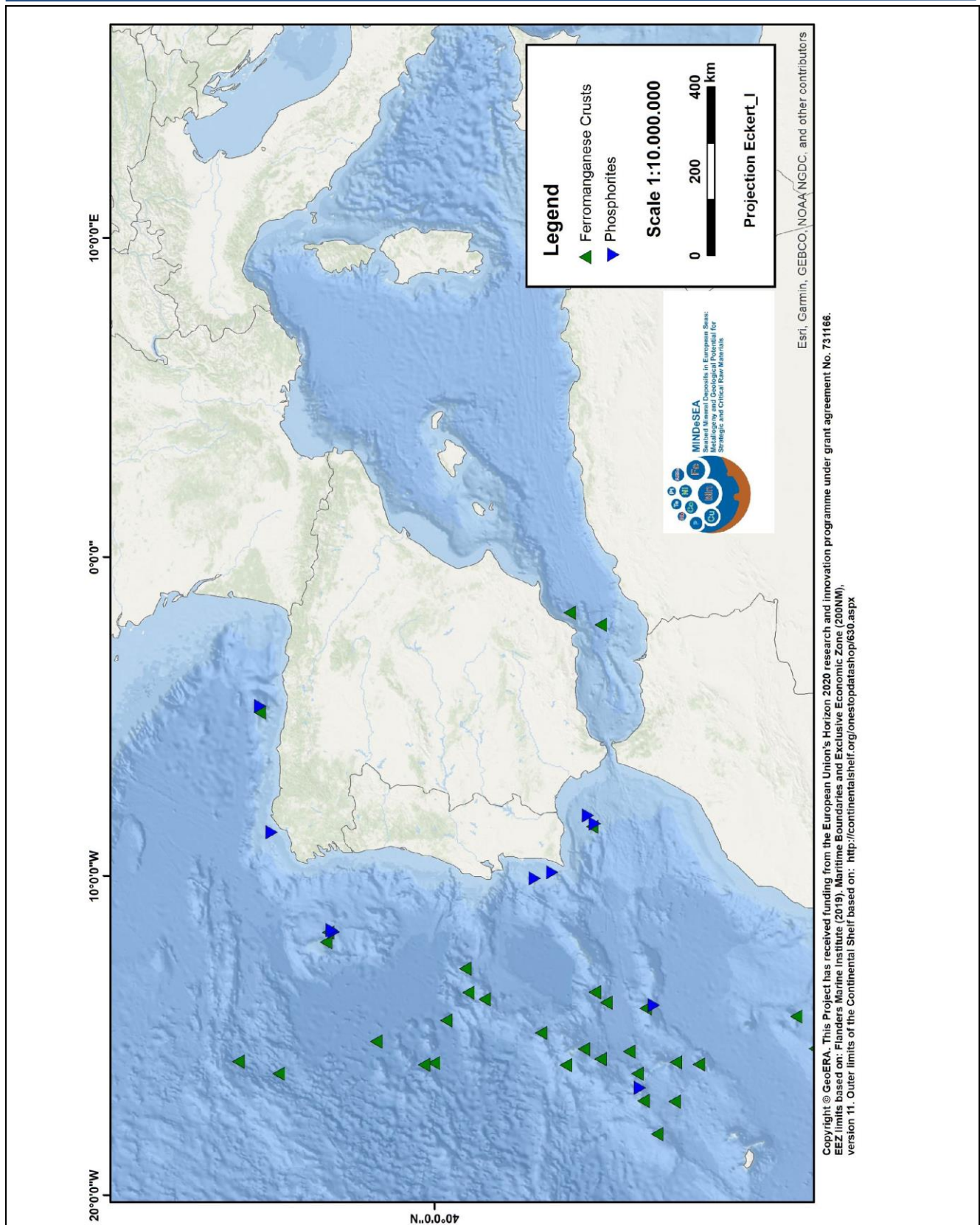


Figure 13. Location of ferromanganese crust and phosphorite occurrences in the Bay of Biscay and Iberian coast.

3.2.5 North East Atlantic Ocean

The Northeast Atlantic Ocean comprises the area east of the MAR out of the limits of the other sub-regions described before. In this region are seventeen occurrences Fe-Mn crusts many of which are in international waters (**Figs. 11 and 12**). Fe-Mn crusts of this marine region are found on ridges, seamounts and plateaus at different water depths.

3.2.6 Other marine regions

The MINDeSEA database has listed two occurrences that can be found in the Alboran Sea (Western Mediterranean), within the Spanish EEZ, and located on the Al Mansour Seamount and La Polacra Massif at water depth of 1400 and 1000 respectively (**Fig. 13**). Both locations are submarine volcanoes for which in the database there are no data but the probable host rock is basalt.

In the sub-region of the Iceland Sea has been recognized only one occurrence, located near the limits of the Norwegian Sea region at a depth of 1000 m (**Fig. 12**).

Finally, one last occurrence is located in the Celtic Sea, within the limits of the United Kingdom EEZ. This occurrence is found on the Loch Fyne plateau located a few km northwest of Great Britain (**Fig. 12**).

3.3 The MINDeSEA database

The MINDeSEA database for Fe-Mn crusts and phosphorites includes occurrences of mineralizations gleaned from different sources such as cruise reports, government information, private organizations and academic papers. To have a categorical vision of these data, the database will separate the important information into six fields: 1) General Data; 2) Metallogeny; 3) Geochemistry; 4) Economic Data; 5) Environment; 6) Other Data (**Fig. 14**).

The General Data category provides for each occurrence coordinates, country code, administration and marine region, sector, and location. Metallogeny Data category provides information about the mineralization, the age, the host rock, the main metal commodity and other possible byproducts or co-products. The Geochemical Data category includes the contents of the most-important elements of each type of mineralization as oxides for the major elements expressed in percentage, while the trace elements are expressed for the most part in ppm ($\mu\text{g/g}$). The Economic Data category provides information about resources and reserves as well as geochemistry of the analyzed samples if those data are available. The Environment category addresses the presence of possible and different marine fauna related to the different mineral deposit types and finally, the Other Data category provides information about the references for each occurrence.





	Data	FIELDNAME	Format	Information
General Data	OBJECTID	ID	Number	Feature ID. An internally generated identification number for each feature. Automatically generated within shape file.
	Shape	SHAPE	Geometry	Polygon
	Latitude	LATITUDE	Degrees N	Degrees N
	Longitude	LONGITUDE	Degrees W/ Degrees E	Degrees W/ Degrees E
	Country Code	CODE	Text (2)	Two letter country code (see INSPIRE CODE: CountryType)
	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
	Occurrence/Deposit name	OCCURRENCE	Text (40)	Name of occurrence/ deposit
	Mineral Occurrence Type	OCCURR_TY	Text (40)	see INSPIRE CODES: OccurrenceTypeType
Metallogeny	Year of Discovery	YEAR_DIS	Number	2001, 2016, etc
	Year of Database Entry	YEAR_DB	Number	2018, 2019, etc
	Date of Database Update	UPDATE	Date	dd/mm/yyyy (Date of last update of attributes)
	Deposit Group	DEPOSIT_G	Text (100)	Sediment-related deposits, hydrothermal deposits, volcanogenic deposits, magmatic deposits, metamorphism-related deposits (see INSPIRE CODES: DepositGroupType)
	Setting	SETTING	Text (250)	Description of geological setting (see INSPIRE CODE: EventEnvironmentType)
	Geomorphic Features	GEOMORPH	Text (250)	Geomorphology of area of FeMn crust occurrence
	Age	AGE	Text (250)	Age of the mineral deposit and host rock (see INSPIRE CODE: NamedAgeType)
	Host Rock	HOST_ROCK	Text (250)	Substrate rock or sediment surrounding the ore deposit (see INSPIRE CODE: LithologyType)
	Metallic Commodity	METAL_COMM	Text (40)	Including precious and non-precious metals (see INSPIRE CODE: CommodityType)
	Other Metals	OTHER_ME	Text (40)	See INSPIRE CODE: CommodityType
Chemistry	Commodity Group	COMM_G	Text (40)	Base metals, precious metals, energy metals, technological metals (see INSPIRE CODE: CommodityType, parents field)
	Ore Minerals	ORE_MIN	Text (250)	Principal minerals/commodities (see INSPIRE CODE: MineralNameType)
	Gangue Minerals	GANGUE	Text (250)	Non-economic minerals (see INSPIRE CODE: MineralNameType)
	Ore mineral distribution	ORE_DISTR	Text (250)	Brecciated, banded, micro-layered, etc (see INSPIRE CODE: AlterationTypeType)
	Alteration	ALTER	Text (250)	Alteration minerals formed during/after the process of mineralization (see INSPIRE CODES: AlterationDegreeType, AlterationDistributionType, AlterationTypeType)
	Morphology	MORPH	Text (250)	Shape and internal structure (thickness) of the mineral deposit (see INSPIRE CODE: FormType)
	Texture	TEXT	Text (250)	Banded, columnar, mottled, etc
	Geochemistry	GEOCHEM	Text (100)	Link to Geochemistry table
	Number of samples	N	Number	Number of analysed samples
	SiO ₂ %	SiO2__pc	Number	(Do Average concentration, dry wt
Economic Data	TiO ₂ %	TiO2__pc	Number	(Do Average concentration, dry wt
	Al ₂ O ₃ %	Al2O3__pc	Number	(Do Average concentration, dry wt
	Fe ₂ O ₃ %	Fe2O3__pc	Number	(Do Average concentration, dry wt
	MnO %	MnO__pc	Number	(Do Average concentration, dry wt
	MgO %	MgO__pc	Number	(Do Average concentration, dry wt
	CaO %	CaO__pc	Number	(Do Average concentration, dry wt
	Na ₂ O %	Na2O__pc	Number	(Do Average concentration, dry wt
	K ₂ O %	K2O__pc	Number	(Do Average concentration, dry wt
	P ₂ O ₅ %	P2O5__pc	Number	(Do Average concentration, dry wt
	Co %	Co__pc	Number	(Do Average concentration, dry wt
Other Data	Ni %	Ni__pc	Number	(Do Average concentration, dry wt
	Cu %	Cu__pc	Number	(Do Average concentration, dry wt
	Zn (ppm)	Zn_ppm	Number	(Do Average concentration, dry wt
	Nb (ppm)	Nb_ppm	Number	(Do Average concentration, dry wt
	Mo (ppm)	Mo_ppm	Number	(Do Average concentration, dry wt
	Li (ppm)	Li_ppm	Number	(Do Average concentration, dry wt
	Sc (ppm)	Sc_ppm	Number	(Do Average concentration, dry wt
	V (ppm)	V_ppm	Number	(Do Average concentration, dry wt
	Bi (ppm)	Bi_ppm	Number	(Do Average concentration, dry wt
	Te (ppm)	Te_ppm	Number	(Do Average concentration, dry wt
Environment	W (ppm)	W_ppm	Number	(Do Average concentration, dry wt
	Pd (ppb)	Pd_ppb	Number	(Do Average concentration, dry wt
	Pt (ppb)	Pt_ppb	Number	(Do Average concentration, dry wt
	Rh (ppb)	Rh_ppb	Number	(Do Average concentration, dry wt
	Ru (ppb)	Ru_ppb	Number	(Do Average concentration, dry wt
	Tl (ppm)	Tl_ppm	Number	(Do Average concentration, dry wt
	Pb (ppm)	Pb_ppm	Number	(Do Average concentration, dry wt
	Y (ppm)	Y_ppm	Number	(Do Average concentration, dry wt
	La (ppm)	La_ppm	Number	(Do Average concentration, dry wt
	Ce (ppm)	Ce_ppm	Number	(Do Average concentration, dry wt
Other Elements	Pr (ppm)	Pr_ppm	Number	(Do Average concentration, dry wt
	Nd (ppm)	Nd_ppm	Number	(Do Average concentration, dry wt
	Pm (ppm)	Pm_ppm	Number	(Do Average concentration, dry wt
	Sm (ppm)	Sm_ppm	Number	(Do Average concentration, dry wt
	Eu (ppm)	Eu_ppm	Number	(Do Average concentration, dry wt
	Gd (ppm)	Gd_ppm	Number	(Do Average concentration, dry wt
	Tb (ppm)	Tb_ppm	Number	(Do Average concentration, dry wt
	Dy (ppm)	Dy_ppm	Number	(Do Average concentration, dry wt
	Ho (ppm)	Ho_ppm	Number	(Do Average concentration, dry wt
	Er (ppm)	Er_ppm	Number	(Do Average concentration, dry wt
Analytical technique	Tm (ppm)	Tm_ppm	Number	(Do Average concentration, dry wt
	Yb (ppm)	Yb_ppm	Number	(Do Average concentration, dry wt
	Lu (ppm)	Lu_ppm	Number	(Do Average concentration, dry wt
	REY (Total %)	REY__pc	Number	(Do Average concentration, dry wt
	Other Elements	OTHER_E	Text (50)	(add as many fields as needed)
	Analytical technique	TECHNIQUE	Text (50)	Technique used (AAS, ICP-MS, ICP-AES, XRF etc) (see INSPIRE CODE: AnalyticalMethodTypeType)
	Deposit Size	SIZE	Text (100)	Magnitude of the mineral deposit calculated according to ProMine (unknown, occurrence, small, medium, large, very large) (see INSPIRE CODE: ImportanceType)
	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	RESOURCES	Number	Resources in Mt
	Reserves	RESERVES	Number	Reserves in Mt
Economic Data	Mined Tonnage	MIN_T	Number	in Mt
	Total Tonnage	TOTAL_T	Number	in Mt
	Remaining Tonnage	REM_T	Number	in Mt
	Resource Reporting System	RES_REP	Text (40)	PERC, JORC, NI43-101, etc (see INSPIRE CODE: ClassificationMethodUsedType)
	Reference for Tonnage	REF_T	Text (40)	Company ordering the assessment
	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. (see INSPIRE CODE: MineStatusType)
	Operator	OPERATOR	Text (250)	Research, exploration or operating agency/company
	Exploration Type	EXPLOR_TY	Text (250)	Exploration techniques employed to describe the mineral deposit (see INSPIRE CODE: ExplorationActivityTypeType)
	Cruises	CRUISE	Text (250)	Cruises identification
Sampling Methods	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	DEPOS_KM2	No. Double	Area of deposit (Sq. Km)
	Depth to Deposit (m)	DEPTH_TO_D	No. Double	Depth to deposit from sea surface
	Fauna	FAUNA	Text (100)	Type of fauna (e.g. corals,...)
	Description	DESCRIP	Text (500)	Deposit summary and metallogenic 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)
Other Data	Comments	COMMENTS	Text (250)	Any additional comments or observations

Figure 14. Overview of the general schema of data for the WP4.



4. METALLOGENY

4.1 Metallogeny of critical raw material in pan-European Seas

In 2020 the European Commission published the actualized Critical Raw Materials (CRMs) list in which the attention is focused on 30 elements (plus 15 REE and 5 PGM) in which four of them, bauxite, lithium, titanium, strontium, are new with respect to the previous 2017 list (**Fig. 15**) (European Commission, 2020a).

2020 critical raw materials (new as compared to 2017 in bold)		
Antimony	Hafnium	Phosphorus
Baryte	Heavy Rare Earth Elements	Scandium
Beryllium	Light Rare Earth Elements	Silicon metal
Bismuth	Indium	Tantalum
Borate	Magnesium	Tungsten
Cobalt	Natural graphite	Vanadium
Coking coal	Natural rubber	Bauxite
Fluorspar	Niobium	Lithium
Gallium	Platinum Group Metals	Titanium
Germanium	Phosphate rock	Strontium

Figure 15. EC 2020 Critical Raw Materials List.

The European economy and industry depend on importation of most of these elements, for example from China (REY), Turkey (borate) and Africa (PGE), with the risk that the supply of these elements could suffer stops or a significant increase of price. This is why the EU commission is focusing in finding and evaluating CRM deposits within its own boundaries (European Commission, 2020b).

In the marine environment it is possible to find deposits and/or occurrences that contain several of these elements, each of which is linked to a particular mineral deposit. Fe-Mn crusts concentrate several interesting and critical elements such as Mn, Ti, Co, Ni, Cu, Te, V, Mo, PGE, and REY among others (Hein et al., 2000; 2013; González et al., 2016; Marino et al., 2017; Marino 2000), while phosphorite concentrates essentially critical elements such as P, F, V, Sr, and REY (Hein et al., 2016; González et al., 2016). Both of these mineral deposits can be found in pan-European seas where they have been differentiated in several metallogenic areas depending on local conditions and genetic processes (**Figs. 16 and 17**).

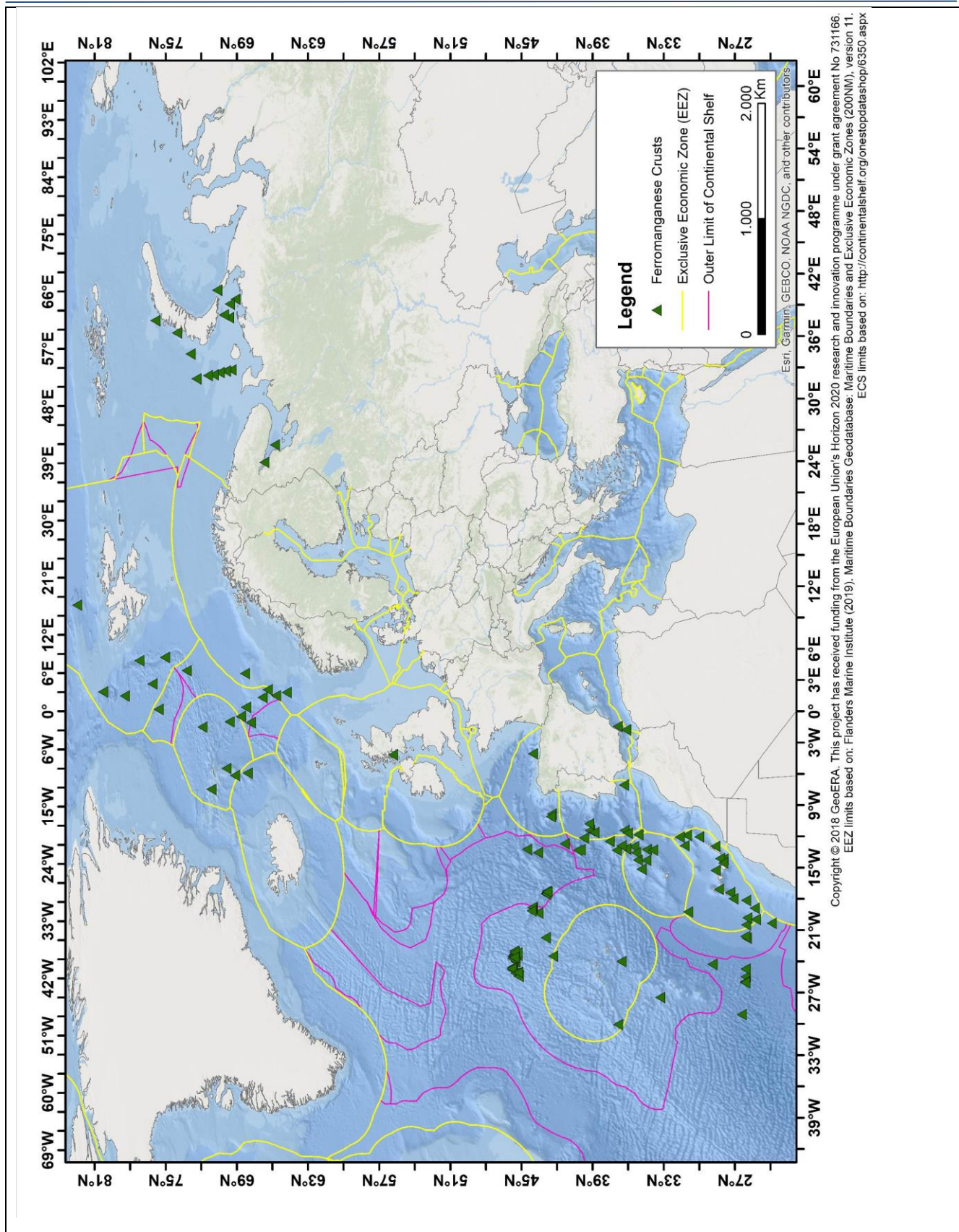


Figure 16. General situation of ferromanganese crusts enriched in CRM in pan-European seas. MINDeSEA dataset and cartography compilation.

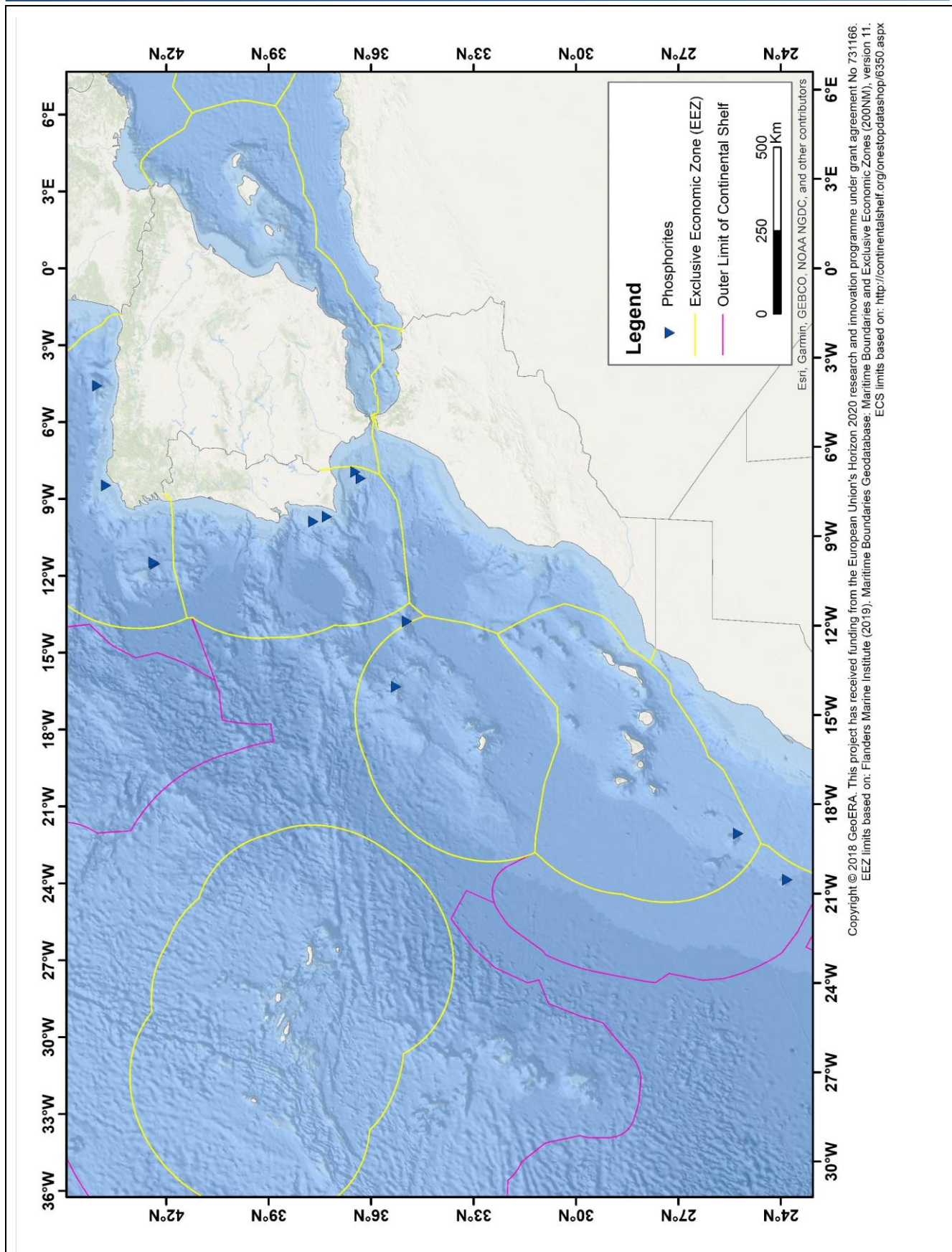


Figure 17. General situation of phosphorites enriched in CRM in pan-European seas. MINDeSEA dataset and cartography compilation.

4.2 Metallogeny of Mn and Fe

Mn and Fe are highly concentrated in Fe-Mn crusts with contents between 18 and 22 % forming the main minerals of this type of deposit. Manganese and associated elements accumulate in the oxygen minimum zone (OMZ) and subsequently form Mn-oxides and Fe-oxyhydroxides by direct precipitation from cold waters when (Koschinsky and Halbach, 1995; Hein et al., 1997; 2000; Marino et al., 2017). Mn and Fe are not included in the 2020 CRMs list but their value as base metals and their high contents in Fe-Mn crusts warrant consideration as coproduct of crust mining.

The main Mn minerals in Fe-Mn crusts are vernadite (or Fe-vernadite) that is a hydrogenetic phyllomanganate with a 7 Å reflection, formed by sheets of octahedrons of MnO_6 separated by an interlayer in which can be found water molecules and other ions. These ions are absorbed due to the presence of a negative charge in the octahedral layer due to deformation and vacancies (Post, 1999; Manceau and Combes, 1988; Manceau et al., 1997; 2014). Other phyllomanganates are also found in some Fe-Mn crusts including birnessite (also 7 Å) and asbolane and busserite (diagenetic minerals with a 10 Å basal reflection). Mn oxides also have minerals in which the octahedral chains form a tunnel structure such as romanechite and todorokite. This structure allows incorporate of large ions (Mg, Ni, Ba, etc.) that may give the mineral better stability (Post, 1999; Manceau and Combes, 1988; Manceau et al., 1997; 2014). On the other hand, Fe minerals are represented essentially by X-ray amorphous phases that include goethite, and metastable ferrihydrite and ferrixyhyte. These minerals show a positive charged structure that allow the absorption of several other elements such as Ti, V, heavy REE (HREE), etc. (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003). These minerals incorporate several critical and strategic elements (Co, Ni, Cu, Mo, V, Ba, Tl, Ti, REY, etc.) both in the structure (substituting Mn with Co, Ni, etc.) and within the interlayer with high contents (i.e., Co up to 1 %, REY up to 0.4 %) (Hein et al., 2000; González et al., 2016; Marino, 2020).

4.3 Metallogny of Ni and Cu

Fe-Mn crusts concentrated several metals in their structure that are not included in the CRMs list but that are economically important. Ni and Cu are not critical elements, but they are considered strategic elements due to their industrial uses. Ni is essentially linked in part to the presence of diagenetic Mn minerals (todorokite, busserite, asbolane), which can concentrate up to 6%, although, bulk hydrogenetic Mn-oxides typically only average about 0.3% Ni that could be considered as a byproduct (Hein et al., 2000; González et al., 2016; Marino et al., 2018; 2019) (Fig. 18). Cu is also concentrated in diagenetic Mn minerals with contents up to 2% while bulk hydrogenetic crusts typically have only 0.10% Cu, which is linked to both the Mn and Fe phases) (Koschinsky and Hein, 2003; Hein et al., 2013; Marino et al., 2018; 2019).



4.4 Metallogeny of Co

Co is one of the essential elements in Co-Li batteries that are the most important part of the new generation of Electric Vehicles (EVs), but is also used in several steel alloys, as pigment and one of its isotopes (^{60}Co) is used as sterilizer of medical equipment, cancer radiation treatment, and for industrial radiography of buildings. There are different marine Co minerals deposits/occurrence that can be found in pan-European Seas, and usually are associated with different morpho-tectonic structures depending on the deposit type. Cobalt occurrences in marine deposits can be divided into primary and secondary types. Both types are linked to the formation of iron and manganese oxides deposits and are Fe-Mn crusts and polymetallic nodules. Fe-Mn crusts represent the primary type and concentrate the highest contents of Co as they form on rock outcrops on seamounts, ridges and plateaus and are formed by the slow accretion of Fe and Mn oxyhydroxides floccules with growth rates of 1-5 mm/Ma (Hein et al., 1997; 2000; 2013; González et al., 2016; Marino, 2020). The enrichment of Co, up to 1%, is due to the slow sorption from seawater (Co^{2+}) that is directly oxidized (Co^{3+}) on the surface of the hydrogenetic Mn oxides, predominantly vernadite and birnessite that show some charge due to vacancies and torsion of the mineral structure (Post, 1999; Hein et al., 2000; Marino et al., 2019; Marino, 2020). The largest deposits of Fe-Mn crusts on these hard surfaces are related both to the presence of currents, that have to be strong enough to keep them clear from sediments but not too strong to erode the freshly precipitated minerals (Bogdanov et al., 1995), and the presence of a thick Oxygen Minimum Zone (OMZ) in which several elements, Co among them, are concentrated and slowly absorbed on the oxide structure (Hein et al., 2000; Pohl et al., 2011).

In Europe Fe-Mn crusts deposits can be found in several regions: (i) in the Macaronesia there is the highest concentration of this deposit type linked to the presence of a great number of seamounts and ridges; (ii) in the Iberian Margin Fe-Mn crusts are linked essentially to the presence of plateaus and some shallow seamounts; (iii) in the North Atlantic in the Norwegian Sea linked to the presence of several ridges; and finally, (iv) in the Barents and Kara Seas can be found as encrustations on the top of the sediments (**Fig. 16**)

4.5 Metallogeny of REY

REY are essential in the development of new and green technologies and are highly coveted by European industries; supply of REY is essentially focused on China for exportation (98 %) (European commission, 2020b). REY deposit and occurrences are linked to the presence of different marine minerals and deposits such as Fe-Mn crusts, polymetallic nodules, and phosphorites (Baturin, 1982; Hein et al., 2000; 2013; González et al., 2016; Marino, 2020).

REY can be found dissolved in seawater as mono- and di-carbonate complexes and concentrated on the surface of Mn oxides and Fe oxyhydroxides of Fe-Mn crusts and nodules depending on their charge. Light REE (LREE) form mono-carbonates with positive charge that concentrate on the surface of the negatively charged hydrogenetic Mn minerals such as vernadite and birnessite. HREE plus Y, on the other hand form di-carbonates complexes with negative charge that are essentially linked to the positive Fe oxyhydroxides (Byrne and Lee, 1993; Koschinsky and Halbach, 1995; Hein et al., 1997; 2000) (**Fig. 18**).



Marine phosphorites also concentrated interesting amounts of REY in their mineral structure and these elements can be extracted as by and/or co-products of the phosphate mining. Marine phosphorites can be found in three main environments: continental margin (CM) (essentially in shelf, slopes, banks, etc.), old seamounts, and in lagoon or insular deposits (Hein et al., 1993; 2016; Glenn et al., 1994; González et al., 2016). REY are concentrated in phosphorites essentially in the carbonate fluorapatite, in which they substitute for Ca in the francolite lattice (Jarvis et al., 1994; Piper, 1999). LREE enter substituting for Ca in the Ca2 positions while HREY enter in the phosphorite structure substituting Ca in its Ca1 position; elements like Eu and those with a similar radius don't have any preference for Ca1 or Ca2 sites (Hughes and Rakovan, 2015; Hein et al., 2016). Moreover, HREE plus Y (%HREY) are highly enriched in phosphorites with respect to other REE deposits such as crusts and nodules, with the %HREY for continental-margin phosphorites reaching an average value of 49% while seamount phosphorites have an average of 60% and can reach 79% of the total REY (Hein et al., 2016; González et al., 2016).

4.6 Metallogeny of P

Mining phosphate is an essential commodity used in agriculture as fertilizer and is essential in order to satisfy the increasing food demand of the growing population. For this reason, the European Commission expects that prices of phosphate/phosphorus will grow about 2% in the global market (European Commission, 2015).

The main mineral deposits for phosphorus are phosphorites and phosphate rocks in which is essentially a main part of the apatite structure with average P contents of around 8-12 % (Gaspar, 2000; González et al., 2016; Marino et al., 2017). The great demand of this element makes Europe an importer with an average of 4 million tons per year of phosphate minerals (European Commission, 2015). Moreover, EU also could extract several other elements as byproducts of the metallurgy of phosphorites, among them are REY but also F and Sr that have high mean contents (respectively 2-3 % and 1200-2000 µg/g) (Hein et al., 2016; González et al., 2016).

The principal phosphorite deposits are linked to the CM, seamounts, and lagoon/islands environments. In the pan-European Seas are CM and seamount types associated with the Iberian margin and with the seamounts of Macaronesia (Fig. 17).

4.7 Metallogeny of PGM, V, W, Te, and Li

PGM are in the list of the critical raw material for their multiple uses both as chemical and automotive catalysts (substituting heavy and toxic metals), but also in their medical and electronic applications and fuel cells. The source of these elements is dominated by South Africa (84%) and Russia (European Commission, 2020a). A comprehensive work on Pt in crusts and nodules was published recently (Koschinsky et al., 2020), which discusses the various proposed mechanisms of enrichment of Pt, and shows a range in Pt contents of 44 to 3207 ng/g. That multi-method study showed that Pt is enriched via an sorption-oxidation mechanism on only the Mn-oxide phase in hydrogenetic crusts and nodules—Pt is a hydrogenetic metal, and is less abundant in nodules with a diagenetic component because Pt is very low in the sediment diagenetic pore fluids. Pt contents

can be enhanced in phosphatized crust under conditions that are different from diagenetic input to nodules. Recent studies made on Fe-Mn crusts from Macaronesia show an enrichment of these elements with respect the continental crust of 10^2 to 10^3 times and contents between 130 and 520 ng/g (average 300 ng/g) (Marino, 2020).

Vanadium is also concentrated in Fe-Mn crusts in the Fe and Mn oxyhydroxides but is highly concentrated in the FeOOH phase (60%) with respect to the MnO₂ phase (40%) (Koschinsky and Hein, 2003; Marino et al., 2018). This particular behavior of V is due to its present in natural environment both as vanadyl ion (VO₂⁺) that could enter in the structure of the negatively charged vernadite and birnessite, but also as vanadate ions (HVO₄²⁻) that are linked to the positive charged amorphous FeOOH (Jeandel et al., 1987; Bayssse et al., 2000; Koschinsky et al., 2003). Contents of V in Fe-Mn crusts of the area range between 400 and 3000 µg/g with an average content of 900 µg/g (Muiños et al., 2013; González et al., 2016; Marino et al., 2017; Marino, 2020). V is also present in phosphorites where can be found both with the apatite and clay minerals (McKelvey et al., 1953; Medrano et al., 1998; Hein et al., 2000). Geochemical analysis made on Iberian margin phosphorites show contents of 150 µg/g that could be extracted as a byproduct of the main element (González et al., 2016).

Tungsten is dissolved in seawater as an oxy-anion species (WO₄²⁻) (Turner et al., 1981; Strekopytov, 1996; Sohrin et al., 1999; Lutfi Firdaus et al., 2008). The concentration of W in Fe-Mn crusts is strictly dependent on the presence of the positive charge on the surface of the FeOOH (Koschinsky and Hein, 2003; Bauer et al., 2017). Although W has low contents in the studied Fe-Mn crusts with values from 30 to 140 µg/g, average 70 µg/g, its enrichment in Fe-Mn crusts can reach 10^6 to 10^8 times its content in continental crust. The importance of W is its uses in several aeronautic, space and defense alloys, also in alloys used in technology and for its uses in several tools (mills, cutters and mining) (European Commission 2020a).

Tellurium is found dissolved in seawater due to a scavenging-type distribution at the ocean surface, predominantly Te(VI), and strong scavenging at depth by particulate matter, with a predominance of a factor of 2 to 3.5 compared with the more stable Te(IV) (Lee and Edmond, 1985; Hein et al., 2003). Tellurium speciation in seawater is not completely understood, it is usually found as HTeO₃⁻ and H₅TeO₆⁻ complexes and are usually sorbed on the positively charged surface of the Fe oxyhydroxides (Lee and Edmond, 1985; Hein et al., 2003). The model proposed involve the sorption of Te (IV) on the Fe minerals and its subsequent oxidation to a more stable Te(VI) (Hein et al., 2003). However, Te can sorb to the Mn-oxide phase and co-precipitate with the Fe oxyhydroxide (Kashiwabara et al., 2014). Te is the element of Fe-Mn crusts that show the highest enrichment if compared with its mean in continental crust, ranging between 10^5 and 10^4 times more enriched (Hein et al., 2003). Tellurium is used in synthetic organic chemistry in several processes that involve protecting group, and is of global interest to be used for high-performance photovoltaic cells for solar panels as a CdTe alloy.

Finally, lithium is present in low contents in hydrogenetic crusts and nodules (around 80 µg/g), but high-resolution analyses reveal that diagenetic minerals in Fe-Mn crusts and nodules can concentrated up to ten times more Li (200 to 900 µg/g and an average of 660 µg/g) (Muiños et al., 2013; Marino et al., 2019).



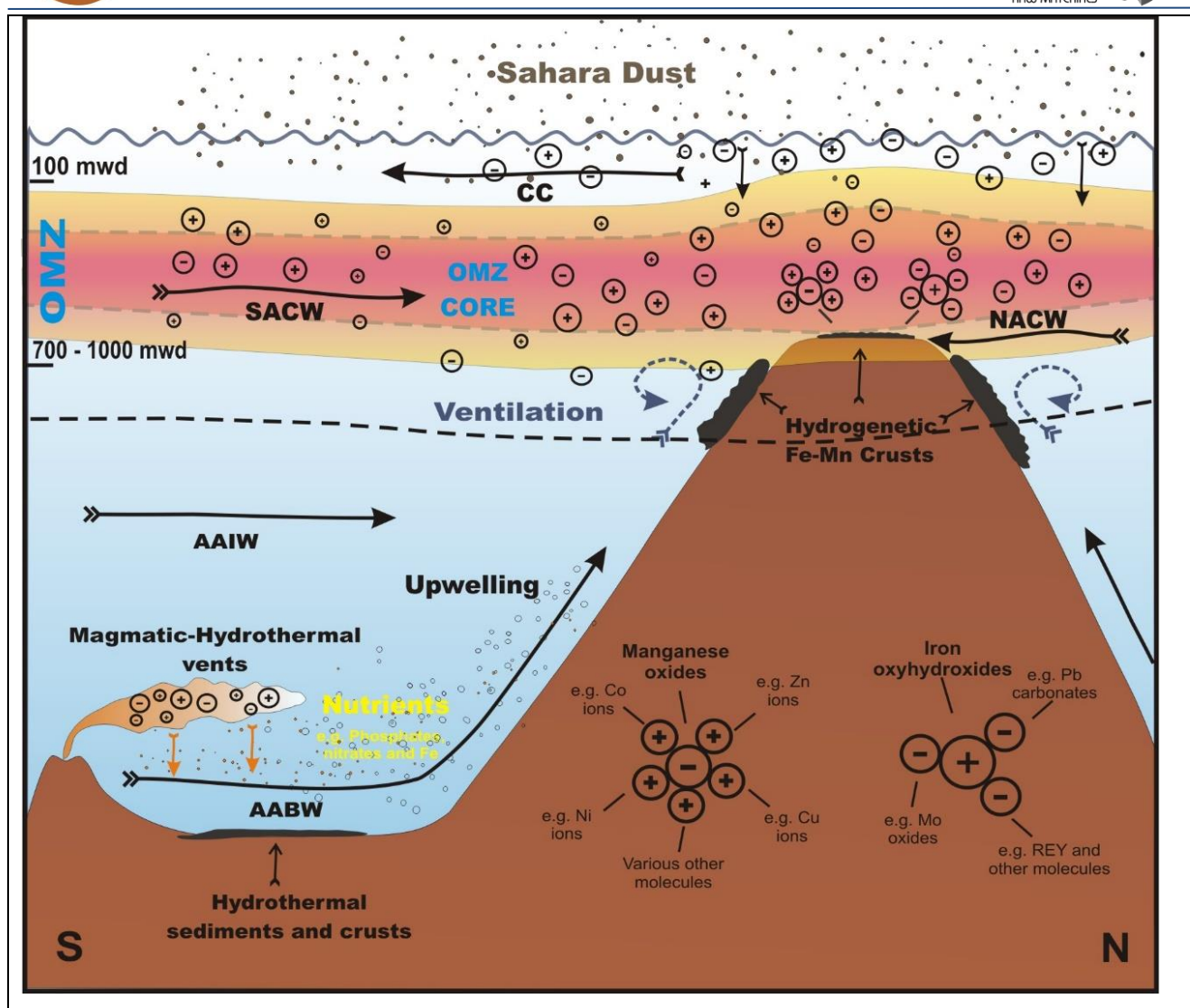


Figure 18. Schematic representation of the Fe-Mn crusts in which the different factors influencing their formation (OMZ, currents, hydrothermal influence, dissolved elements) and the different elements associated with the Fe and Mn (oxyhydr)oxides (Marino et al., 2017).

4.8 Metallogeny of Ti, Nb, Hf and Sb

Titanium is important due to its uses in several metal light and strong alloys especially for the aeronautic, space and defense industries and for several medical application (implants, pacemakers, etc.) (European Commission 2020a). Titanium can be found dissolved in seawater as titanium hydroxide and is integrated in the Fe-Mn structure both as a surface complex on the recently precipitated Fe-Mn oxyhydroxides and as surface precipitation of hydrous compounds (Farley et al., 1985; Bau et al., 1996).

Niobium is also used in the creation of several superalloys, but also is used in high-tech applications for the creation of capacitors, superconductors, strong magnets, etc. (European Commission, 2020a). Nb can be found dissolved in seawater both as organic compounds and hydroxide (Carlisle and Hummerstone, 1958; Sohrin et al., 1998) and is accumulated in the Fe-Mn crusts by sorption on the Fe oxyhydroxide.

Importation of hafnium is predominantly from France and USA that together control 90 % of the market. Hf is used in the creations of superalloys and refractory ceramics, but also in the nuclear power plants. On the other hand, the antimony market is essentially controlled by China, even if the major importer for Europe is Turkey (62%). Antimony uses are essentially focused in defense applications and lead-acid batteries (European Commission, 2020a). Both Sb and Hf are acquired through sorption on the Fe oxyhydroxide in Fe-Mn crusts.

All these elements can be found in Fe-Mn crusts linked to the presence of the slightly positively charged surface of the amorphous FeOOH phase. These elements are enriched in Fe-Mn crusts deposits with respect the continental crust, Ti is the most enriched (10^8 - 10^{10} times) while Nb, Hf, and Sb are enriched 10^6 - 10^8 times (Hein et al., 2000; Koschinsky and Hein, 2003). In pan-European Fe-Mn crusts Ti can be found with contents between 0.2 and 2.4 % (Muiños et al., 2013; González et al., 2016; Marino, 2020). Nb was also studied in several European deposits reporting contents varying between 40 and 150 µg/g (Muiños et al., 2013; Marino et al., 2017). Compared to Ti and Nb, Hf and Sb contents are slightly lower (respectively average 10 and 40 µg/g) (Muiños et al., 2013; González et al., 2016; Marino, 2020). Although contents of these elements are not very high, their concentration in Fe-Mn crusts warrant consideration as byproducts of the metallurgy of other elements such as Co and Mn (Hein et al., 2013; Koschinsky et al., 2018).

5. METALLOGENETIC MODELS AND PROVINCES

Different marine minerals that have attracted the attention of industry can be found from coastlines to deep-ocean basins. The theory of plate tectonics (Wegener, 1929) increased our knowledge about marine mineral resources, mostly with regard to deposits that have been found in the deep-ocean basins and in the Area (Rona, 2003; 2008). The principal plate tectonics and other minor plates play a key role for mineralization processes. Divergent plate boundaries such as the mid-ocean ridges, show multiple magmatic, volcanic, and hydrothermal manifestations. These divergent plate-borders represent around 60.000 km in the world.

Following De Launay (1913), the term ‘metallogenic province’ was defined by Hawkes and Webb (1962) as a domain on the Earth with an unusual abundance of ores of a particular metal or type (e.g. Cu province of Chile). ‘metallotect’ was in fact introduced first by Laffitte et al. (1965) and defined as “any geological feature or phenomenon associated with lithology, paleogeography, structure, geochemistry, etc. which has contributed to the formation of a mineral concentration”. A metallotect is generally defined as a specific tectonic, geological, mineralogical or geochemical feature which hosts mineral deposits and played a key role in controlling their formation.

Accordingly, ISA regulations on ferromanganese crusts exploration:

- Metallogenic provinces that are potential ore-bearing large volcanotectonic and dome-shaped uplifts of the ocean floor, usually located along the boundaries of the abyssal basins;

- Metallogenic regions that are fragments of metallogenic provinces, located within concrete volcanic-tectonic structures and domes with directly proven prospects for ore potential of the crustal type;
- Metallogenic fields – fragments of ore regions, confined to individual guyots with abundant cobalt-bearing ferromanganese crusts, studied in great detail, with subsequent assessment of their qualitative and quantitative characteristics;
- Minerals deposits – accumulations of cobalt-bearing ferromanganese crusts, whose reserves and quality satisfy the requirements for commercial exploitation;
- Mineral occurrences- presumably local accumulations of cobalt-bearing ferromanganese

5.1 Fe-Mn crusts genetic models

According to the International Seabed Authority (ISA, 2012), “cobalt crusts” are defined as hydroxide/oxide deposits of cobalt-rich iron/manganese (ferromanganese) crusts formed by direct precipitation of minerals from seawater onto hard substrates, containing minor but significant concentrations of Co, Ti, Ni, Pt, Mo, Te, Ce, other metallic and REEs (ISA, 2012) (**Fig. 19**).

Ferromanganese crusts occur globally throughout the ocean and on seamounts, ridges and plateaus where currents have kept the rocks swept clean of sediments for millions of years (e.g., Koschinsky et al., 1996; Hein et al., 1997; 2000; 2013; Rona, 2008). The first discovery of these types of deposits was in the south of the Canary Islands during the HMS Challenger cruises in the late nineteenth century (Murray and Renard, 1891).

Marine Fe-Mn deposits are usually classified in three mineralization types depending on the predominant genetic process acting during their growth: hydrogenetic, hydrothermal, and diagenetic forming commonly crusts, nodules, or stratabound deposits (Hein et al., 2000).

5.1.1 Hydrogenetic model

The hydrogenetic model includes the direct precipitation from cold ambient seawater of colloid floccules of Mn-oxides and Fe oxyhydroxides (Halbach, 1986; Hein et al., 1997; 2000; Koschinsky and Halbach 1995; Koschinsky and Hein 2003). The main minerals in hydrogenetic deposits are essentially low-crystallinity Mn phyllosulfates represented essentially by Fe-vernadite and birnessite, intergrown with low-crystallinity and amorphous Fe-oxyhydroxides represented by goethite group minerals and metastable phases as feroxyhyte and ferrihydrite (Glasby, 1972; Hein et al., 1997; 2000). All these minerals show a surface charge due to structural deformation and vacancies that have to be balanced with the interaction of different hydrated cations such as Co, Ni, Zn, Sn, and Ce are, for example, attracted by the negatively charged surfaces of colloidal hydrous Mn-oxide particles, whereas hydrated anions and elements forming larger complexes with low-charge densities (e.g. U, As, Pb, Hf, Th, Nb, and REEs) are attracted by the slightly positively charged hydrous Fe-oxyhydroxide particles (Halbach et al., 2017). These micrometric floccules accumulate on hard substrates between 250 and 7500 m depth during millions of years, showing a growth rates of 1-5 mm/Ma (Hein et al., 2000). These very slow growth rates and the presence of charged

surfaces allow hydrogenetic Fe-Mn crusts to incorporate and be enriched in many elements dissolved in seawater (Hein et al., 2000; Koschinsky and Hein, 2003). Between critical and strategic elements, the highest enrichments are for Co, Ni, Te, V, Mo, REYs and Pt (respectively up to 8000, 4500, 60, 850, 500, 3500 µg/g and 560 ng/g) (Hein et al., 2000; 2013; Muiños et al., 2013; Marino et al., 2017). In pan-European seas can be recognized two main metallogenic provinces: (i) Macaronesia; (ii) Norwegian Sea; that will be discussed further.

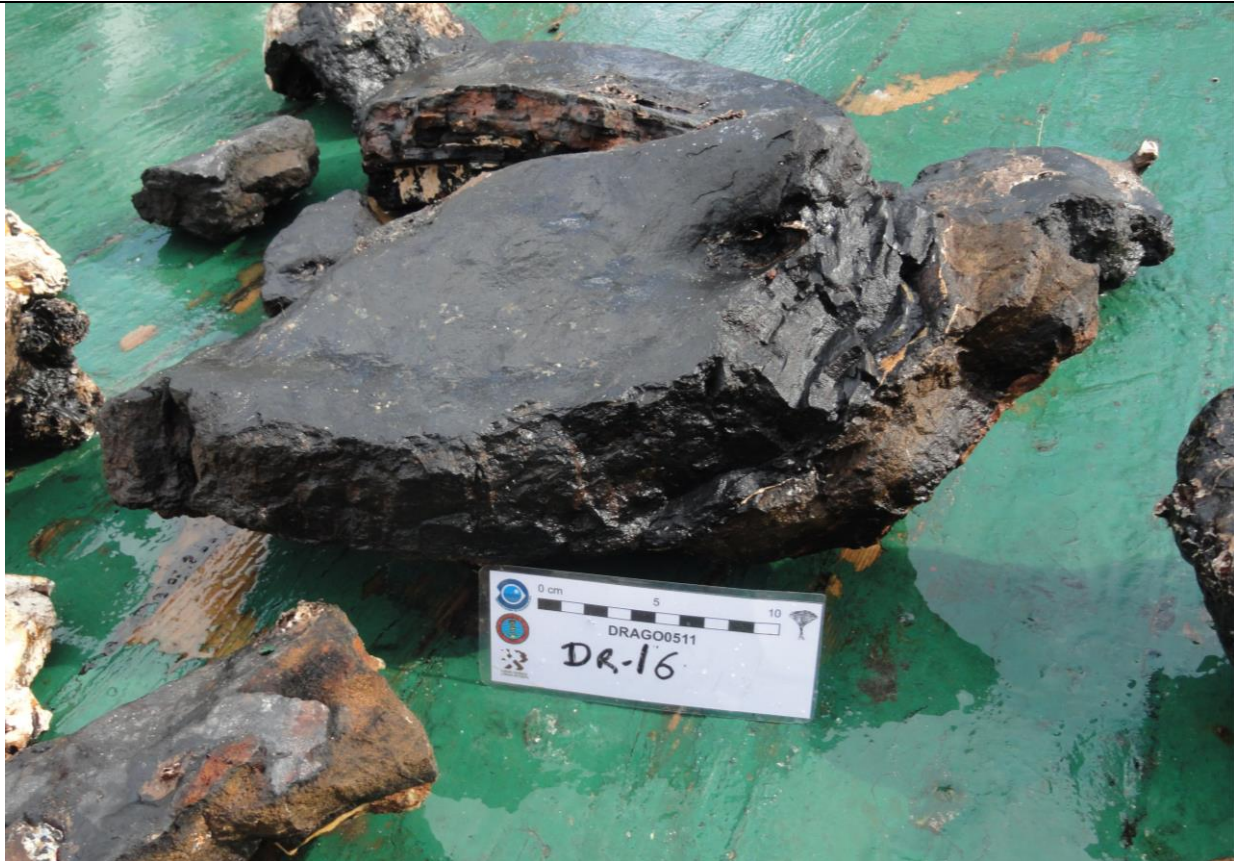


Figure 19. Samples of thick cobalt-rich ferromanganese crusts recovered from Tropic Seamount (Canary Islands). DRAGO 0511 Expedition. Photo: IGME.

5.1.2 Diagenetic model

The diagenetic model involves precipitation and accretion of Fe and Mn minerals during early diagenesis in the sediment under suboxic conditions (Halbach et al., 1988; Kuhn et al., 2017). These processes occur within the sediment pore waters at depth typically between 5-30 cm in the sediment column (Halbach et al., 1988; Wegorzewski et al., 2014; Kuhn et al., 2017). Furthermore, a completely different type of diagenetic process occurs under suboxic conditions during phosphatization--carbonate-fluorapatite impregnation, which may cause partial dissolution and reprecipitation of Mn minerals (Halbach et al. 2008). Diagenetic minerals are represented by two main categories of Mn minerals: tectomanganates (todorokite incorporating Mn^{3+} , Ni^{2+} , Mg and Ba) and phyllosilicates (buserite and asbolane incorporating multiple divalent and trivalent metallic cations), both formed by octahedral layers of MnO_6 , but with different structures as previously was described (Chukhrov et al. 1979; Post et al. 2003; Bodeř et al. 2007; Kuhn et al., 2017; Post and Bish

1988; Manceau et al. 1997, 2014; Kuhn et al., 2017). Diagenetic minerals are enriched in Mn, Ni, Cu, Co, Li and Zn (Respectively up to 40, 6, 2 % and 2000, 250 and 4000 µg/g) (Hein et al., 1997; 2000; González et al., 2016; Kuhn et al., 2017; Marino et al., 2018; 2019). In the studied area can be defined two diagenetic provinces, one linked to the shallow waters of the Barents and Kara seas and the other linked to the Iberian Margin deposits.

5.1.3 Hydrothermal model

Finally, hydrothermal processes depend on the direct precipitation of Mn-oxide and Fe-oxide-hydroxide minerals by predominantly hydrothermal precipitation at oceanic spreading axes, midplate volcanic edifices, and volcanic arcs where stratabound or metalliferous sediments due to the circulation of hydrothermal fluids that leach metals from volcanic rocks (Puteanus et al. 1991; Stoffers et al. 1993; Hein et al., 1987; 1995; 1997). These deposits are characterized by a large fractionation between Fe and Mn, and the oxide minerals can be enriched in one or more of Li, Mo, Zn, Pb, Cu, or Cr and in rare cases in Co, Cu, Ni, Hg and Ag (Hein et al., 1997; 2005; González et al., 2016). In several Fe-Mn crusts from the CISP, it has been possible to identify the presence of hydrothermal input to thin laminae both at the base, in contact with altered rock, or through the laminations (Marino et al., 2019; Marino, 2020). Hydrothermal Fe-Mn minerals will be described in the WP3 metallogenic reports on hydrothermal mineralization.

5.2 Phosphorites genetic models

Phosphorites are defined as rocks enriched in phosphorous, usually expressed as P_2O_5 , with contents ranging 15-37 wt. %, with an enrichment reaching 160 times more with respect the continental crust. Scientific community is still investigating on the mechanism that allow the formation of these mineralization's types especially taking into account that dissolved phosphorous shows relatively low concentration in seawater (in average 70 ng/g) (Glenn and Robert, 1978) (Fig. 20).

5.2.1 Authigenic formation

Phosphorus accumulates in bottom waters by the decomposition of the organic material, which can be scavenged by clay minerals and oxyhydroxides but could also accumulate forming diagenetic deposits (Kudrass et al., 2017). In upwelling zones, the great presence of organic matter from the surface productivity generates a suboxic and anoxic environments in which part of this organic matter is consumed by sulfide-oxidizing bacteria, that maintain phosphorus in their cells and could release high concentration of phosphates when there are changes in water conditions, promoting formation of authigenic minerals or more commonly mineralization of carbonate sediments and rocks. These phosphorites are usually formed by carbonate fluorapatite (McCellan and Gremillion 1980; Kudrass et al., 2017).



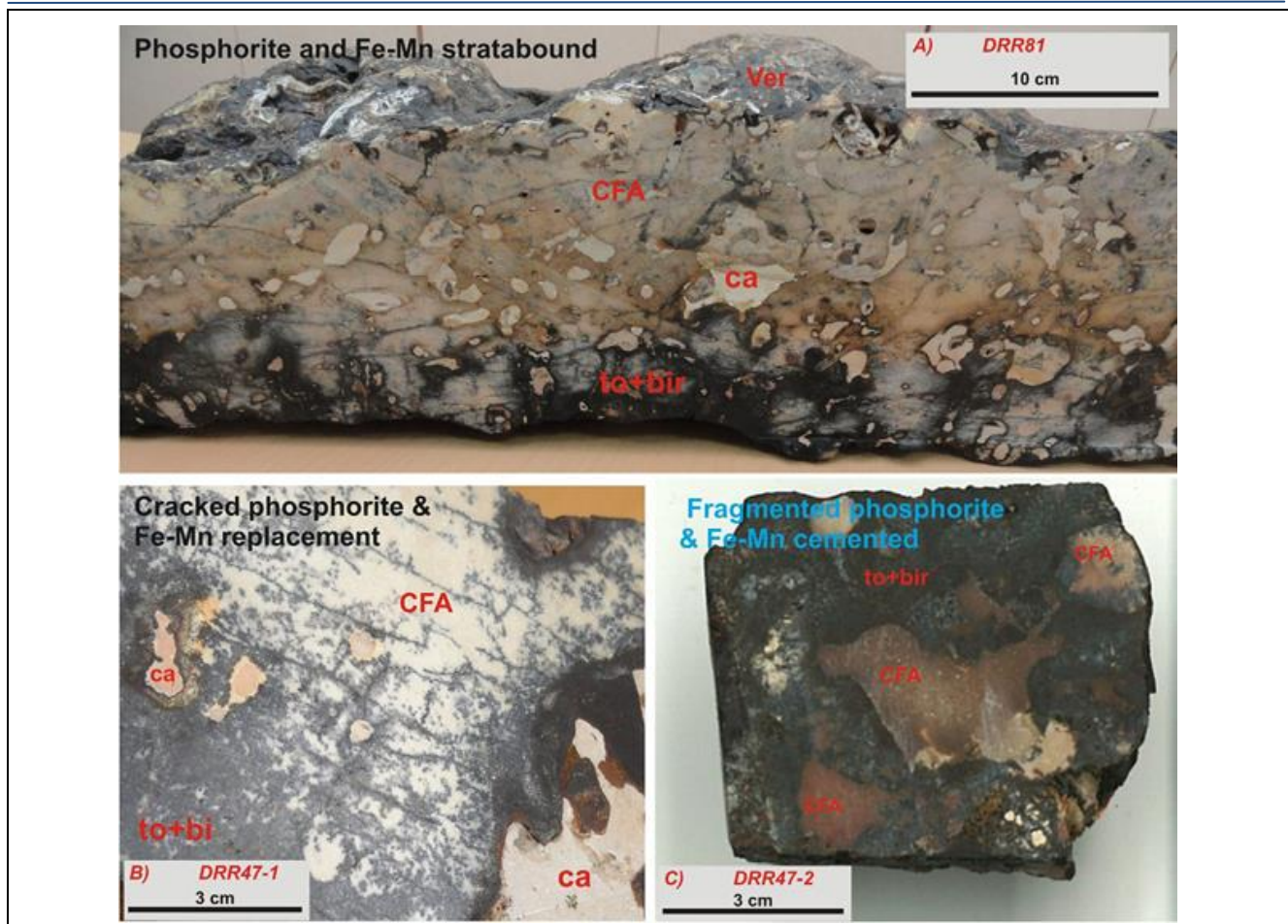


Figure 20. Samples of phosphorite pavement sections with Fe-Mn replacements and stratabound mineralization recovered on the Galicia Bank. DIVA ARTABRIA II Expedition. Photo: IGME.

5.2.2 Diagenetic formation

On the other hand, diagenetic phosphorite forms when the released phosphorus replaces previously formed carbonate biogenic material, forming irregular deposits. These diagenetic processes may also fractionate the REY and enrich them in the CFA; the diagenetic fluid that contributes to the formation of the phosphorite is less enriched in REY compared to seawater unaltered by these diagenetic reactions (Hein et al., 2016). The morphologies of these deposits are usually slabs and cobbles and can also generate authigenic glauconite, dolomite, and pyrite within the sediments (Birch 1980; Kudrass et al., 2017).

5.3 Fe-Mn crusts metallogenic provinces

5.3.1 Macaronesia

In the Macaronesia area have been recognized hundreds of knolls and seamounts with significant Fe-Mn crust pavements. These seamounts are located in the south west of the Iberian Margin but also around the three archipelagos formed by Azores, Madeira, and Canary Islands and on the Mid

Atlantic Ridge. In this area have been recovered several Fe-Mn crusts with average contents of Co of 0.35 % and up to 0.79 % (Muiños, 2015; Merle et al. 2018; Marino 2020).

The case of the Canary Island Seamounts Province (CISP) is very singular showing a high economic potential for Macaronesia. The area encloses more than a hundred seamounts and submarine hills in the Spanish EEZ that are considered an ancient “hot-spot” track in the Atlantic Ocean (**Fig. 21**). These old seamounts (Cretaceous age i.e. Tropic, Las Hijas, The Paps) from the Central Atlantic (van den Bogaard, 2013) cover an area of 24,000 Km² and are covered with extensive pavements of brown to black Fe-Mn crusts with subparallel laminations and thickness from a patina to up to 25 cm (i.e. Marino et al., 2017; 2018; 2019; MINDeSEA, 2020). The seamounts rise from up to 5000 m depth and their summits vary from 200 to 1500 m depth. The main mineralogy of the CISP Fe-Mn crusts is represented by Fe-vernadite and goethite with also small contents of birnessite, busserite/asbolane and todorokite. The geochemistry of the crusts is dominated by Fe and Mn (around 18-22%) and highly enriched in several strategic elements between which the most important for their economic value are Co, Ni, Cu, Mo, REY, Te and PGM (respectively in average 5000, 2300, 600, 450, 3000, 40 µg/g and 250 ng/g). High resolution analysis using point analyses on Fe-vernadite shows the highest contents of Co and REY with up to 1.7 % and 0.5 % respectively (Marino, 2020). Geochemical analyses have been plotted on several graphs in order to identify their genesis, and the results of all these plots (Bonatti et al., 1972; Dymond et al., 1984; Bau et al., 2014) (**Figs. 22A, B and 23A, B**) show that CISP Fe-Mn crusts are hydrogenetic. Moreover, crust ages using the cobalt chronometer and Os isotopes range from 90 to 20 (Tropic Seamount samples) indicating very slow growth rates (1-5 mm/Ma), typical of hydrogenetic Fe-Mn crusts. Preliminary mining models show that one square kilometer on the top of the Tropic Seamount could provide a minimum of 220 t of Co but also 9,000 t of Mn, 84 t of Ni and 170 t of REY (Marino, 2020).

5.3.2 North East Atlantic Ocean

From this area has been recovered several Fe-Mn crusts associated with plateaus (420,000 Km²) and ridges (107,000 Km²) distributed from 63°N to 78°N in Norway, Iceland, and Greenland waters (**Fig. 21**). The main mineralogy of these crusts is represented by vernadite and goethite with also high contents of quartz whose origin could be due to glacial debris incorporate within the lamination during growth of the Fe-Mn crusts. These crusts also show a different geochemistry compared to those from CISP, first of all these samples show the highest contents of aluminum-silica elements (mean 16 %) and also lower contents of Fe and Mn (respectively 22 and 12 % means). Trace elements are also depleted compared with CISP, essentially Co, Ni, Cu, Mo and REY (respectively 2300, 2000, 400, 350 and 3000 µg/g) (MINDeSEA, 2020). Studies on the genetic processes in the formation of these samples show that they are generally hydrogenetic (**Figs. 22A, B and 23A, B**).



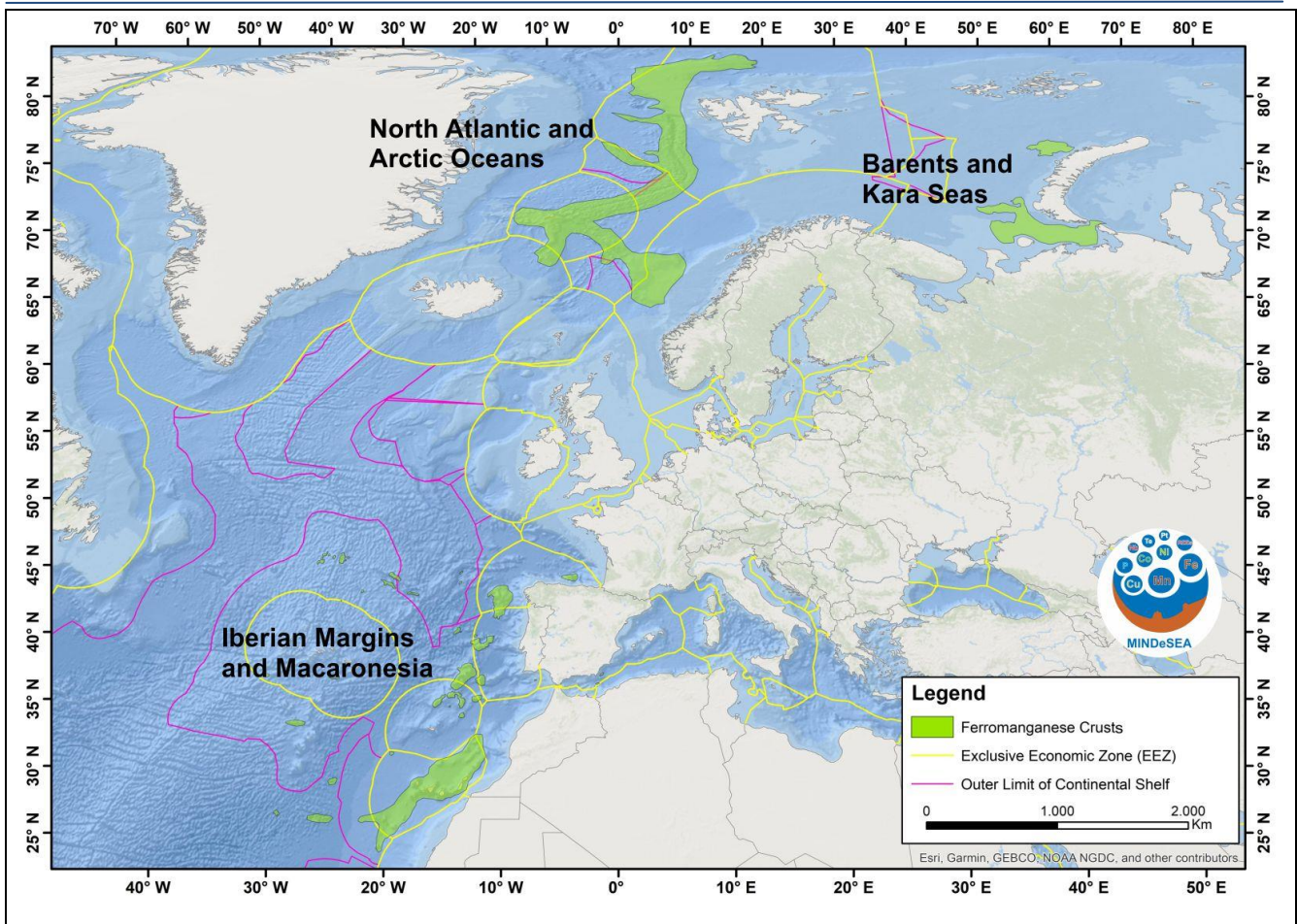


Figure 21. Metallogenic provinces for ferromanganese crusts defined in pan-European seas.

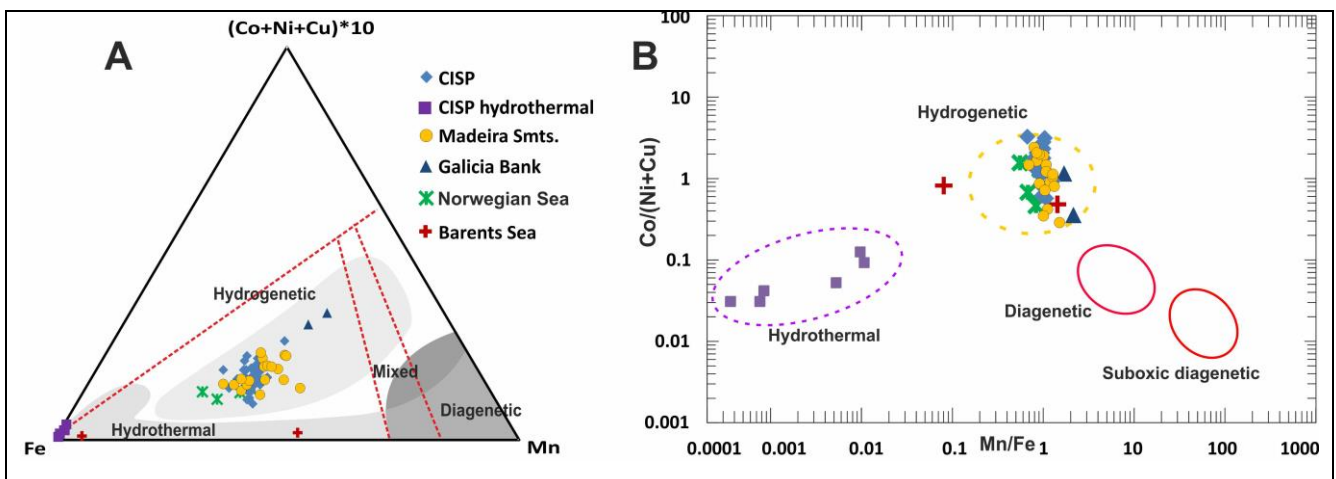


Figure 22. Geochemical data of MINDeSEA samples plotted in A) ternary diagram from [Bonatti et al. \(1972\)](#) and B) binary diagram from [Dymond et al. \(1984\)](#) to differentiate genetic processes of the Fe-Mn crusts.

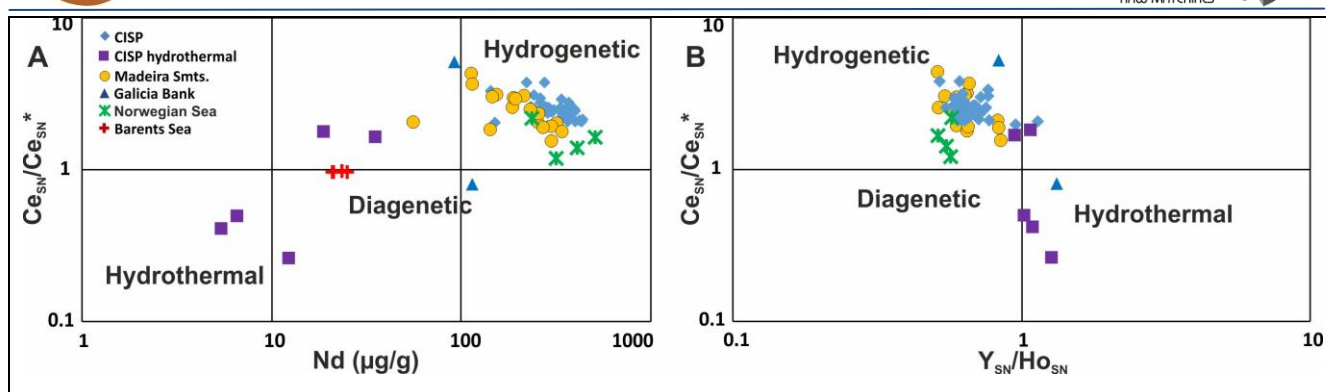


Figure 23. A) and B) plot of REYs indexed on the binary diagram of [Bau et al. \(2014\)](#) in order to differentiate the genetic process involved in their formation.

5.3.3 Barents and Kara seas

The area represents shallow seas of the Arctic Ocean formed above the continental shelf of Russia, with maximum depths of 450 m and an average of 250 m (**Fig. 21**). Several Fe-Mn crusts have been recovered in the area, usually linked to the presence of large shelf areas. Fe-Mn crusts recovered here have a completely different aspect to the deep-sea deposits. These samples form very thin (~ 1 mm) Fe-rich flat or discoidal concretions coatings on rock debris and lithified clay. The mineralogy is dominated by goethite and quartz and the geochemistry show high Fe and Si (respectively up to 20 % and 18 %) with low contents of Mn (~ 10 %). Trace elements are also depleted in these samples with Co, Ni, Cu, Mo and REY (200, 210, 30, 300 and 120 μg/g) ([Ingri, 1985](#); [Strekopytov and Dubinin, 2001](#)). Although if plotted in the ternary diagram from [Bonatti et al. \(1972\)](#) (**Fig. 22A, B**) these samples plot in the hydrothermal field although using REY data ([Bau et al., 2014](#)) these samples properly show a diagenetic origin (**Fig. 23A**) ([Ingri, 1985](#); [Strekopytov and Dubinin, 2001](#)).

The presence of diagenetic laminae was also found in Fe-Mn crusts forming continuous thin lamination in several studied crusts. These laminae, formed by todorokite and buserite/asbolane, are highly enriched in Mn (up to 50 %), Ni (up to 6 %), and Cu (up to 2 %). On the other hand, these laminae are depleted in strategic and critical elements showing low contents of Co, Te and REY (in mean 1000, 3 and 100 μg/g respectively) ([Marino, 2020](#)).

5.3.4 Bay of Biscay and Iberian Coast

All around the Iberian Margin have been recovered Fe-Mn crust samples covering seamounts located at the south (Alboran Sea and Gulf of Cadiz) and the north (essentially Galicia and Le Danois banks). The presence of Fe-Mn crusts in the Alboran Sea and Gulf of Cadiz was confirmed during several cruises but there are scarce studies with which to establish a genetic model for all these Fe-Mn crusts. Ferromanganese micro-crusts from the Cadiz Contourite Channel show a hydrogenetic origin ([González et al., 2012](#)), as with other nearby deposits (Madeira seamounts), we suppose a common hydrogenetic origin (**Fig. 21**).

Galicia Bank is a huge plateau located 150 km to the west of the Spanish coast. This plateau rises from a maximum depth of 5000 to 600 m with an area of 30,000 Km². In this area have been recovered several Fe-Mn samples (both crusts and nodules) but also numerous samples of

phosphorites (González et al., 2016; MINDeSEA, 2020). The studies made on the Fe-Mn crusts show that the mineralogy is dominated by vernadite with the presence of diagenetic Mn minerals (todorokite, romanechite and coronadite). The geochemistry results show high contents of Fe and Mn (respectively 13 and 20 %) but also interesting contents of Co, Ni, Cu, Mo, V (up to 0.85, 0.65, 0.1, 0.03, 0.08 %) but with lower contents of REY (0.1 %) compared with CISP. This difference is due essentially on the genetic processes that formed these crusts that are essentially hydrogenetic with some diagenetic input, this is also confirmed by the presence of diagenetic slabs of phosphorite at the base of the studied crusts (González et al., 2016) (Figs. 22A, B and 23A, B).

5.4 Phosphorites provinces

Whereas the average P_2O_5 content of continental crustal rocks is estimated to be 0.23% and sedimentary rocks average 0.03–0.16%, rocks typically designated as phosphorites have contents ranging from 15 to 37% (Glenn and Robert, 1978).

In Pan-European seas occur phosphorites deposits associated with banks, seamounts, and the continental shelf of the Iberian Margin and Macaronesia. Samples have been recovered in the north of Spain (Galicia) found covering different banks but also to the southwest of Portugal and Spain (Gulf of Cadiz) where they are linked essentially to the shallow continental shelf (Fig. 24). Finally, the presence of phosphorites has been also detected on several seamounts of Macaronesia, in places found at the base or within the lamination of thick Fe-Mn crusts. Phosphorites are interesting deposits due to their high contents of P (between 6 and 13 %) but also due to their enrichment in several REE and Y (in average 1000 $\mu\text{g/g}$ and up to 2000 $\mu\text{g/g}$). Y is the most enriched element with a mean value of 360 $\mu\text{g/g}$ (Marino et al., 2017; Murton et al., 2017).

5.4.1 Macaronesia

Phosphorites can be found covering seamounts in the Macaronesia area (Portugal and Spain) (Fig. 24). Occurrence of these deposits have been found on the Lion and Ampère seamounts, located in the area off south Portugal and Madeira Islands. Other Deposits have been found and studied in the CISP area, at the base of Fe-Mn crusts on Tropic and Echo seamounts. Studies made on these deposits show higher contents of P with respect to the continental shelf samples with an average of 9.8 and up to 11.6 % P. In this area, several other elements have been analyzed between which REY shows an average of 0.08 % with a maximum of 0.15 % (Vázquez et al., 2011; Marino et al., 2017; Murton et al., 2017; MINDeSEA, 2020).

5.4.2 Bay of Biscay and Iberian coast

The occurrences of phosphorites deposits in the Bay of Biscay are associated to the Sancho seamount, Ortegal Terrace, Le Danois Bank, and especially Galicia Bank (Fig. 24). Phosphorites recovered on Galicia Bank show the highest P contents with an average of 13 % and maximum up to 20 % but also high contents of REY with an average of 0.1 % and up to 0.2 %, and the contents of F are also interesting with a mean value of 1.7 %. These samples have been dated as the late Oligocene-early Miocene and formed during three main phosphatization events (González et al., 2016). Extensive deposits of phosphorites, with abundant detrital grains of quartz, feldspar, and clay minerals, frequently encrusted by Fe-Mn oxyhydroxides, and ferrous glauconites were



discovered in the Ortegal Terrace and on Le Danois Bank (Lamboy, 1976; Lucas et al., 1978; Lamboy and Lucas, 1979). The phosphatization process was discontinuous in the space and time since the Miocene to Quaternary times in Cape Ortegal and Le Danois Bank and was driven in all the locations by the diagenetic replacement of carbonate by CFA.

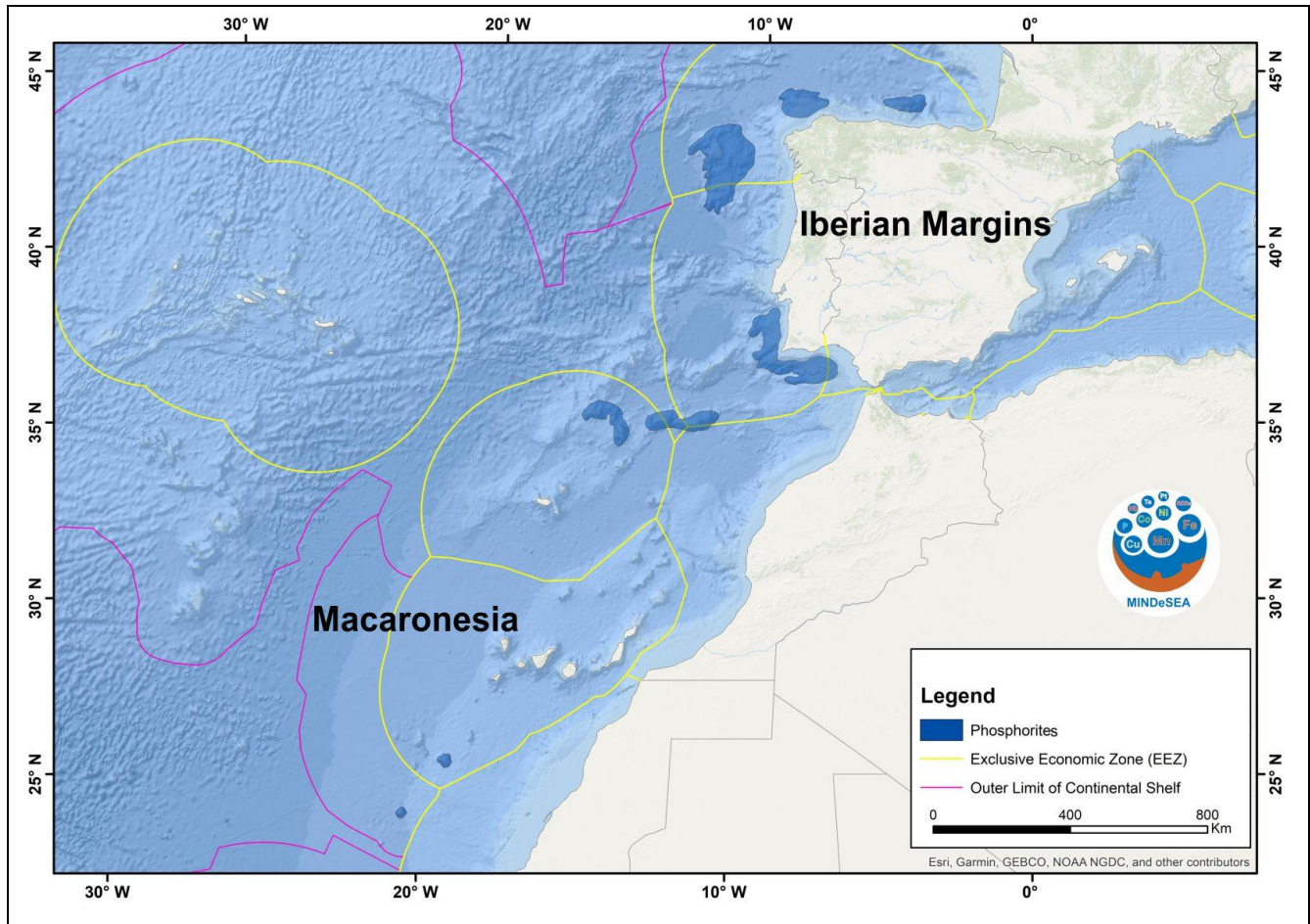


Figure 24. Metallogenic provinces for phosphorites defined in pan-European seas.

In the Gulf of Cadiz phosphorites are located on the continental shelf covering small seamounts and terraces (Fig. 24). Several recovered phosphorites were analyzed and show an average P content of 6.5 % with maximum of 9.4 % (Baturin and Bezrukov, 1971; Baturin, 1982; Gaspar, 1981; 1982; 1986; 2000; Rona, 2008; MINDeSEA, 2020). They are forming part of the East Atlantic Phosphorite Province (Baturin and Bezrukov, 1971).

5.5. Pan-European metallogeny for Co and P: FRAME-MINDeSEA compilation

Data obtained from the MINDeSEA project were also produced in collaboration with the European project FRAME to update and publish the pan-European metallogenic map of CRM (onshore and offshore). These data were used in order to generate pan-European maps both with the mineralization location (Figs. 25 and 27) and metallogeny (Figs. 26 and 28) of the most interesting areas concentrating critical elements such as cobalt and phosphorous. The MINDeSEA project also

collaborates in drafting of related reports and deliverables of the FRAME project ([Forecasting and Assessing Europe's Strategic Raw Materials needs \(FRAME\) – GeoERA](#)).

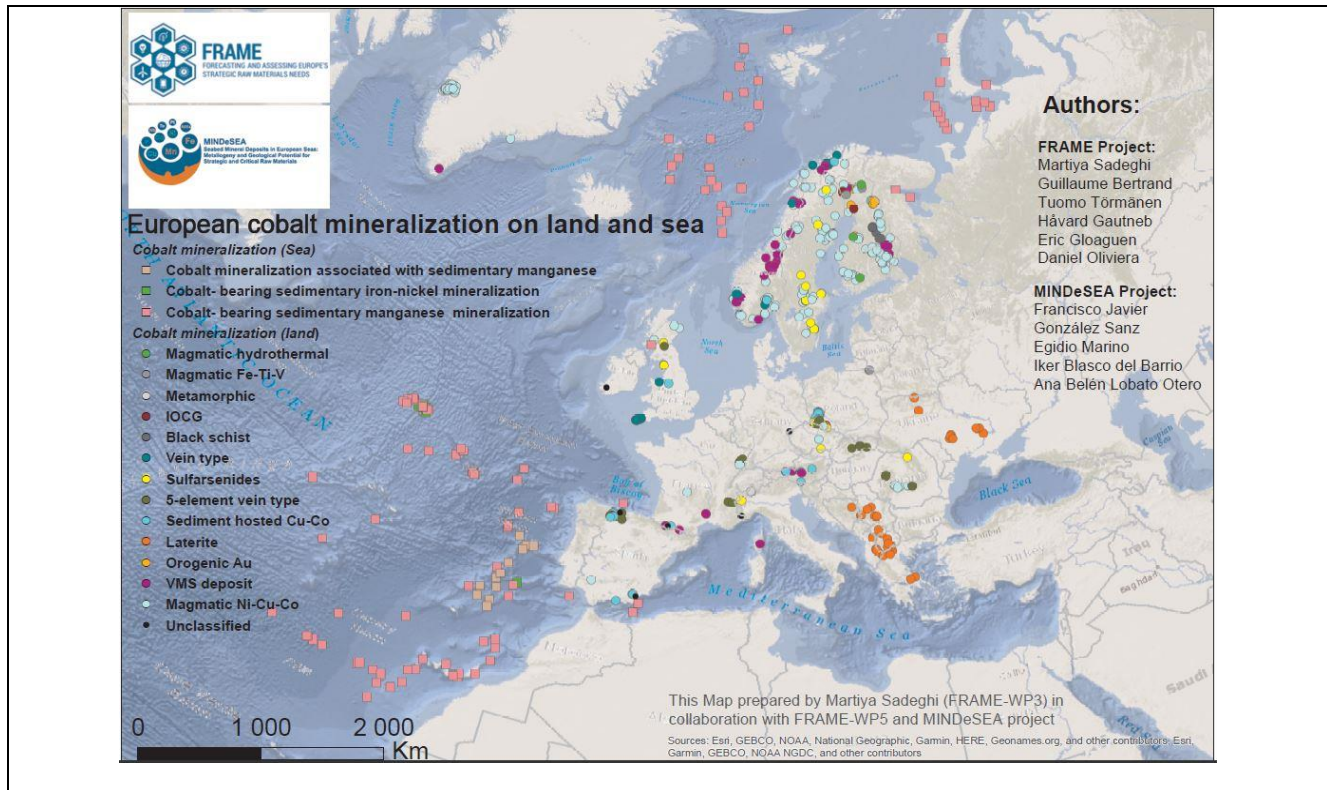


Figure 25. Pan-European map for cobalt mineralization. FRAME-MINDeSEA compilation.

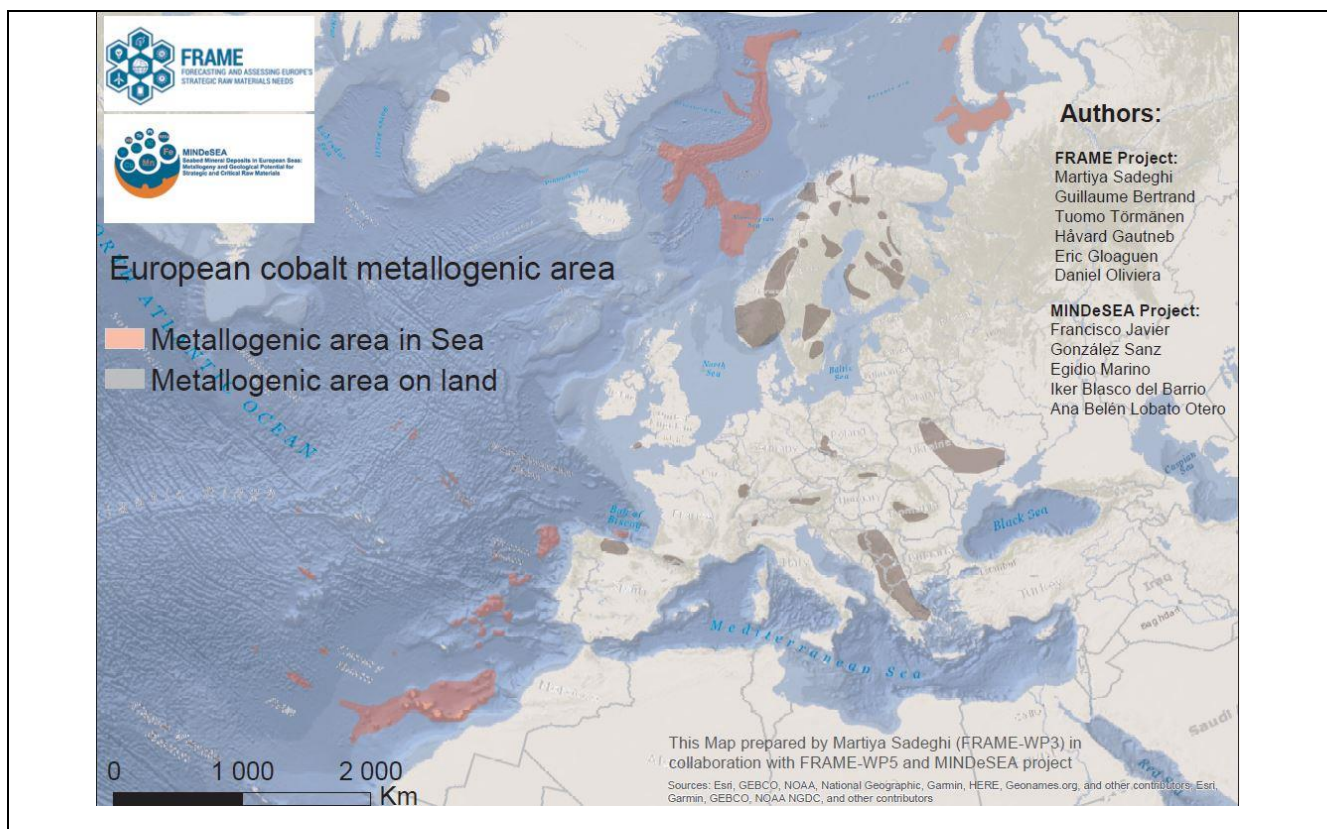


Figure 26. Pan-European map for cobalt metallogenic areas. FRAME-MINDeSEA compilation.

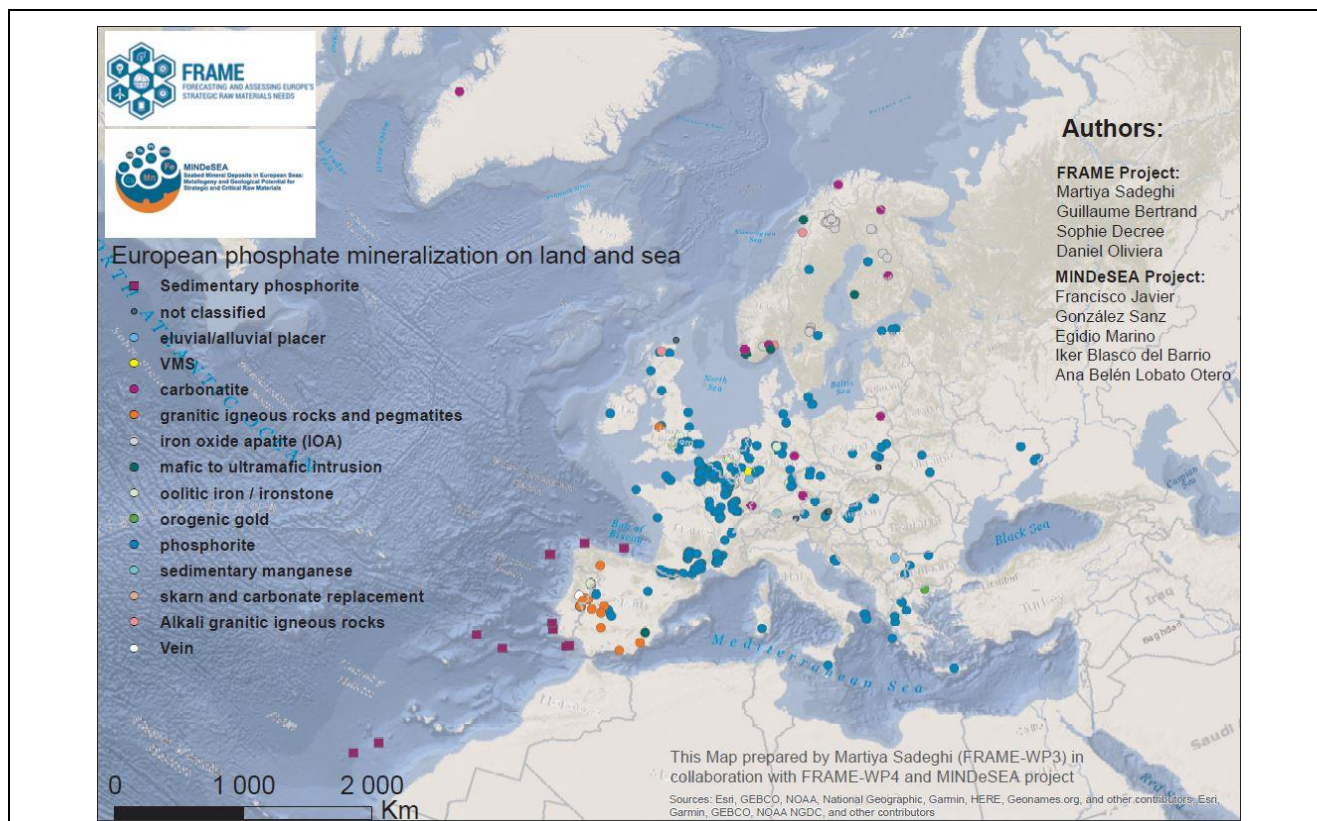


Figure 27. Pan-European map for phosphate mineralization. FRAME-MINDeSEA compilation.

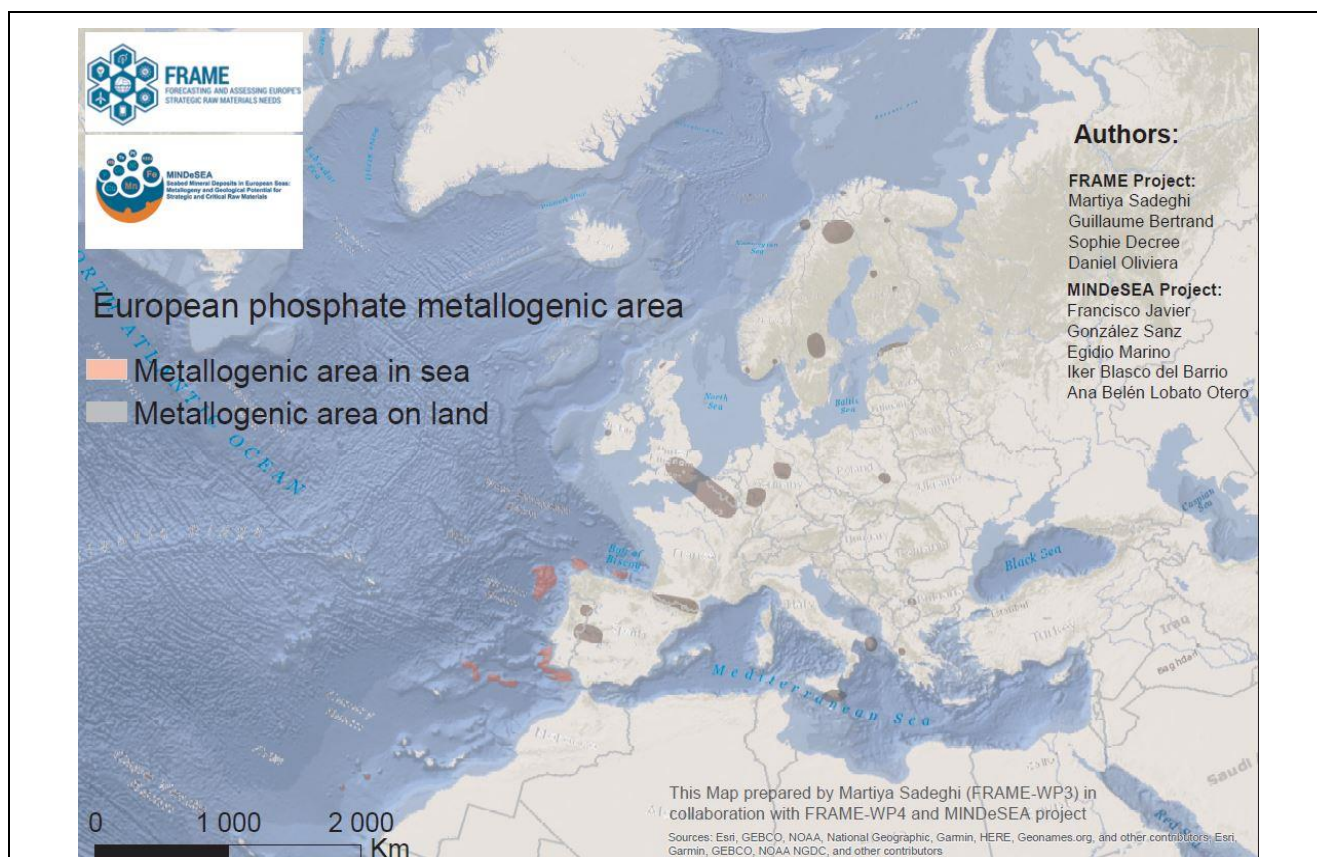


Figure 28. Pan-European map for phosphate metallogenic areas. FRAME-MINDeSEA compilation.

6. FINAL REMARKS

This report provides analytical data from the MINDeSEA database in order to generate metallogenic maps and models for ferromanganese crusts and phosphorites in pan-European seas. This analysis is based on more than 130 bibliographic references, 141 and 12 occurrences of ferromanganese crusts and phosphorites respectively and more than 200 samples analyzed for mineralogical and chemistry.

Fe-Mn crusts and phosphorites are important because they concentrate several CMR both in the main structure of the mineral (e.g. Mn or P) and by sorption from seawater and element substitutions (e.g. Co, Ni, Te, PGM, REY, etc.). In addition, Fe-Mn crusts are deposits that concentrate the highest amount of cobalt even if compared with land-based deposits.

Fe-Mn crusts formed on rock outcrops in the European seas by three main genetic processes: hydrogenetic, diagenetic, and hydrothermal. The hydrogenetic Fe-Mn crusts concentrate the highest contents of the majority of the CRM, essentially Mn, Co, Te, V, Nb, Ti, Pt, and REY. On the other hand, diagenetic Fe-Mn nodules can generate Mn-rich deposits with also high contents of Ni, Cu and Li, while hydrothermal deposits are usually enriched only in Mn or Fe depending of the temperature of the fluids. In shallow seas occur Fe-Mn encrustations enriched in Fe that are formed by diagenetic processes due to low oxygenated waters.

Phosphorites formed by direct precipitation of minerals (essentially carbonate apatite) caused by the entrance of upwelling currents in P-enriched waters or more commonly by diagenetic replacement of carbonates. Phosphorites are enriched in P but also in several CRM as REY, F, and Sr.

Hydrogenetic Fe-Mn crusts due to their slow growth sorb several different elements due to the positive charge of Fe oxyhydroxides and negative charge of Mn oxides. Also, the presence of minerals with laminate or tunnel structure allows for big cations (Co, Ni, Cu, PGEs, etc.) or complexes (e.g., mono- and di- REY carbonates) to be sorbed and oxidized on the previously precipitated Fe and Mn oxyhydroxides.

Based on the data recovered and compiled in the MINDeSEA database it was possible to identify four main metallogenic provinces for Fe-Mn crusts and two provinces for the phosphorites.

The Macaronesia province includes several occurrences localized on slopes and summits of hundreds of seamounts, ridges and submarine hills in that part of the Atlantic Ocean, from the Azores Islands to Canary Islands. In this area, it is possible to highlight the Canary Islands Seamount Province that cover a total area of 24,000 km² distributed on more than 10 major seamounts and banks. CISP Fe-Mn crusts grow by a hydrogenetic process and their mineralogy is dominated by Fe-vernadite and goethite with also small contents of birnessite, buserite/asbolane, and todorokite. This genetic process and mineralogy allow the enrichment of many CRM, such as Co, Ni, Cu, Mo, REY, Te and PGE (respectively in average 5000, 2300, 600, 450, 3000, 40 µg/g and 250 ng/g). The

calculated age for CISP Fe-Mn crusts vary from 90 to 30 Ma, indicating a long history of hydrogenetic growth and promoting enrichment of critical metals.

Bay of Biscay and Iberian Coast metallogenic province includes several Fe-Mn crusts growing on seamounts localized near or on the continental shelf of the Iberian Peninsula. In the north Fe-Mn crusts have been found covering Galicia Bank, a huge plateau with an area of 30,000 km², together with phosphorites slabs. Fe-Mn crusts studied here are formed essentially by hydrogenetic and diagenetic processes and are highly enriched in Co (up to 0.85 wt.%) and also in Ni, Cu, Mo, V (respectively 0.65, 0.1, 0.03, 0.08 wt.%).

In the Northeast Atlantic Ocean is a metallogenic province located in the Norwegian, Iceland, Greenland, and Celtic seas. There is very little information published on Fe-Mn crusts of this area, the few data recovered suggest that they formed by a hydrogenetic process. The contents of the different CRM are a little lower with respect to the Macaronesia samples, probably due to dilution caused by high contents of detrital aluminum-silicates.

Finally, Barents and Kara seas metallogenic province hosts thin Fe-(Mn) encrustations formed essentially by diagenetic processes and with low contents of Co, Ni, Cu, Mo and REY (200, 210, 30, 300 and 120 µg/g).

On the other hand, data for phosphorites recovered up until now allow for delineation of two metallogenic provinces. The Bay of Biscay and Iberian coast province recover phosphorites linked to the continental shelf and the Galicia Bank. In this area phosphorites are highly enriched in P (up to 20 wt.%) and also F and REY (respectively up to 1.7 and 0.2 wt.%). Galicia Bank phosphorites have been dated as late Oligocene-early Miocene.

In Macaronesia, phosphorites cover some seamounts (Tropic and Echo) and occur at the base of the Fe-Mn crusts. These phosphorites have P contents varying from 10 to 12 wt.% but low REY contents (mean 0.08 wt.%).

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8. APPENDIXES



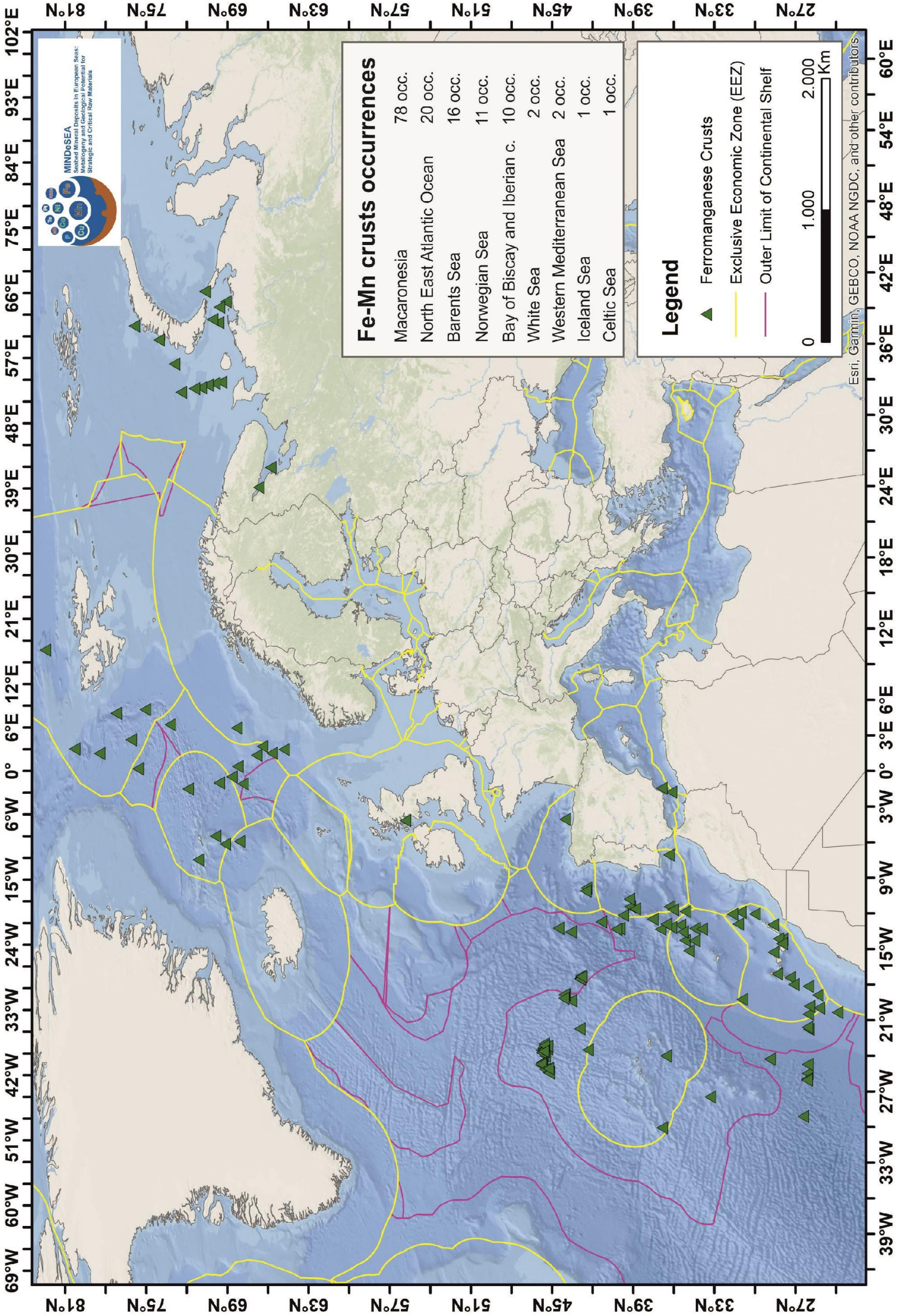
Table 1. Resume of Fe-Mn crusts occurrences for marine regions

Marine region	Occurrences number	Commodity	Principal mineralogy	Genetic model
Macaronesia	78	Mn, Co, REY	Fe-Mn Oxyhydroxides	Hydrogenesis
North East Atlantic Ocean	20	Mn, Co, REY	Fe-Mn Oxyhydroxides	Hydrogenesis
Barents Sea	16	Mn, Co, REY	Fe-Mn Oxyhydroxides	Suboxic diagenesis
Norwegian Sea	11	Mn, Co, REY	Fe-Mn Oxyhydroxides	Hydrogenesis
Bay of Biscay and Iberian coast	10	Mn, Co, REY	Fe-Mn Oxyhydroxides	Hydrogenesis
White Sea	2	Mn, Co, REY	Fe-Mn Oxyhydroxides	Suboxic diagenesis
Western Mediterranean Sea	2	Mn, Co, REY	Fe-Mn Oxyhydroxides	Hydrogenesis
Iceland Sea	1	Mn, Co, REY	Fe-Mn Oxyhydroxides	Hydrogenesis
Celtic Sea	1	Mn, Co, REY	Fe-Mn Oxyhydroxides	Hydrogenesis

Table 2. Resume of phosphorites occurrences for marine regions

Marine region	Occurrences number	Commodity	Principal mineralogy	Genetic model
Macaronesia	4	P, phosphate rock, REY, F	Carbonate Fluorapatite	Diagenesis
Bay of Biscay and Iberian coast	8	P, phosphate rock, REY, F	Carbonate Fluorapatite	Diagenesis



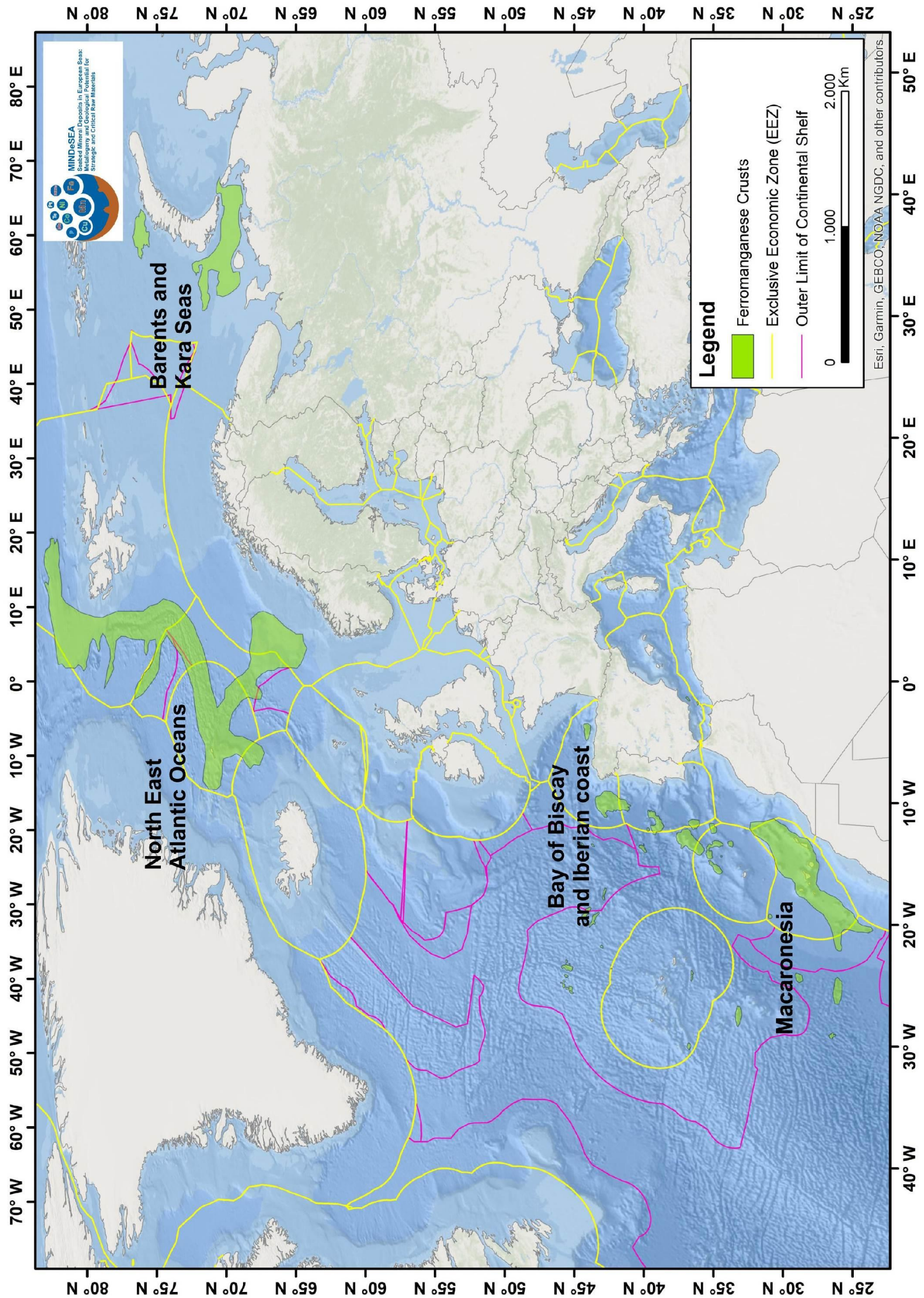


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EEZ limits based on: Flanders Marine Institute (2019). Maritime Boundaries Geodatabase: Maritime Boundaries and Exclusive Economic Zones (200NM), version 11.
ECS limits based on: <http://continentalshef.org/onestopdatasheet/6350.aspx>

Pan-European map of seabed ferromanganese crusts enriched in CRM. MINDeSEA dataset and cartography compilation.

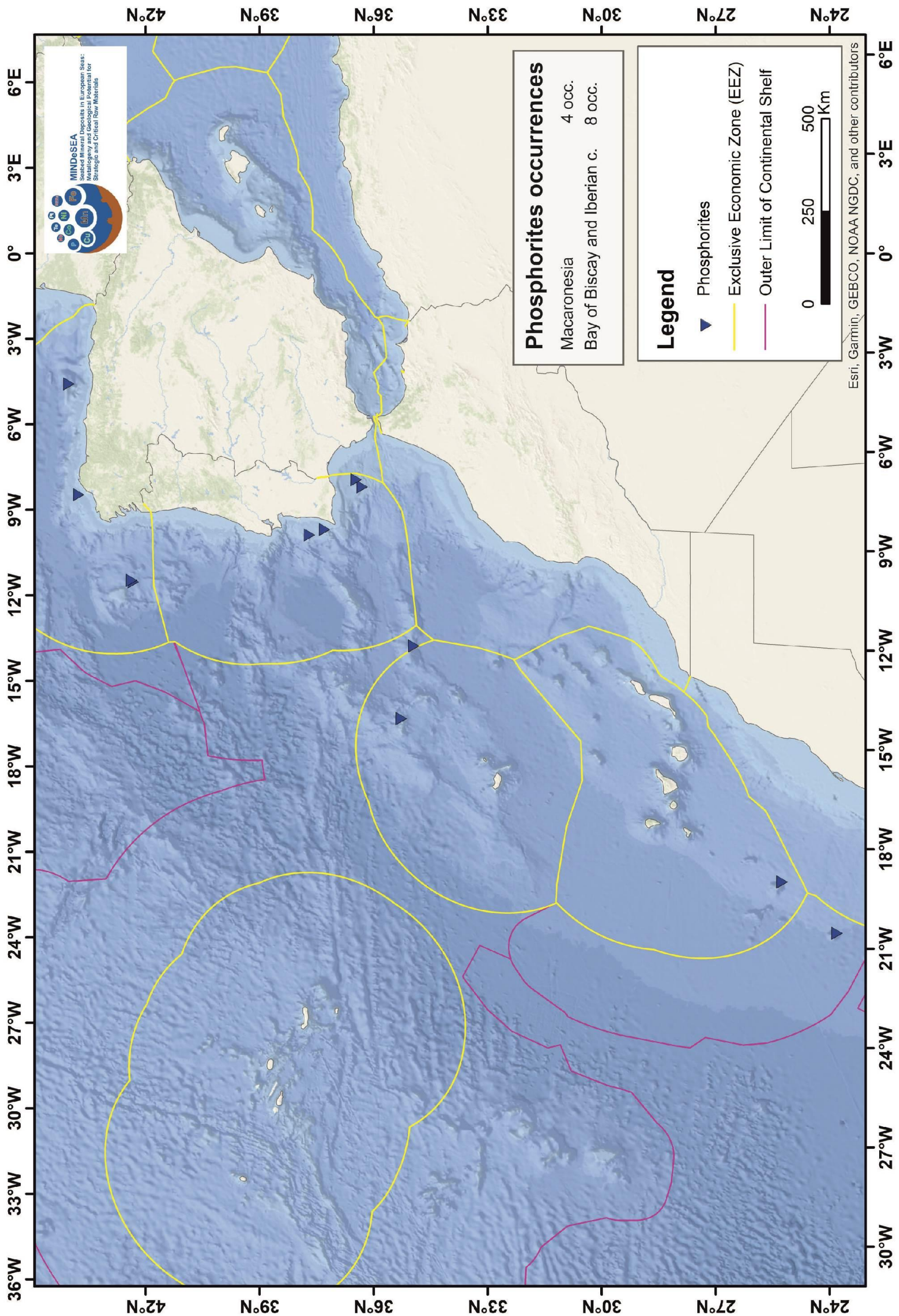


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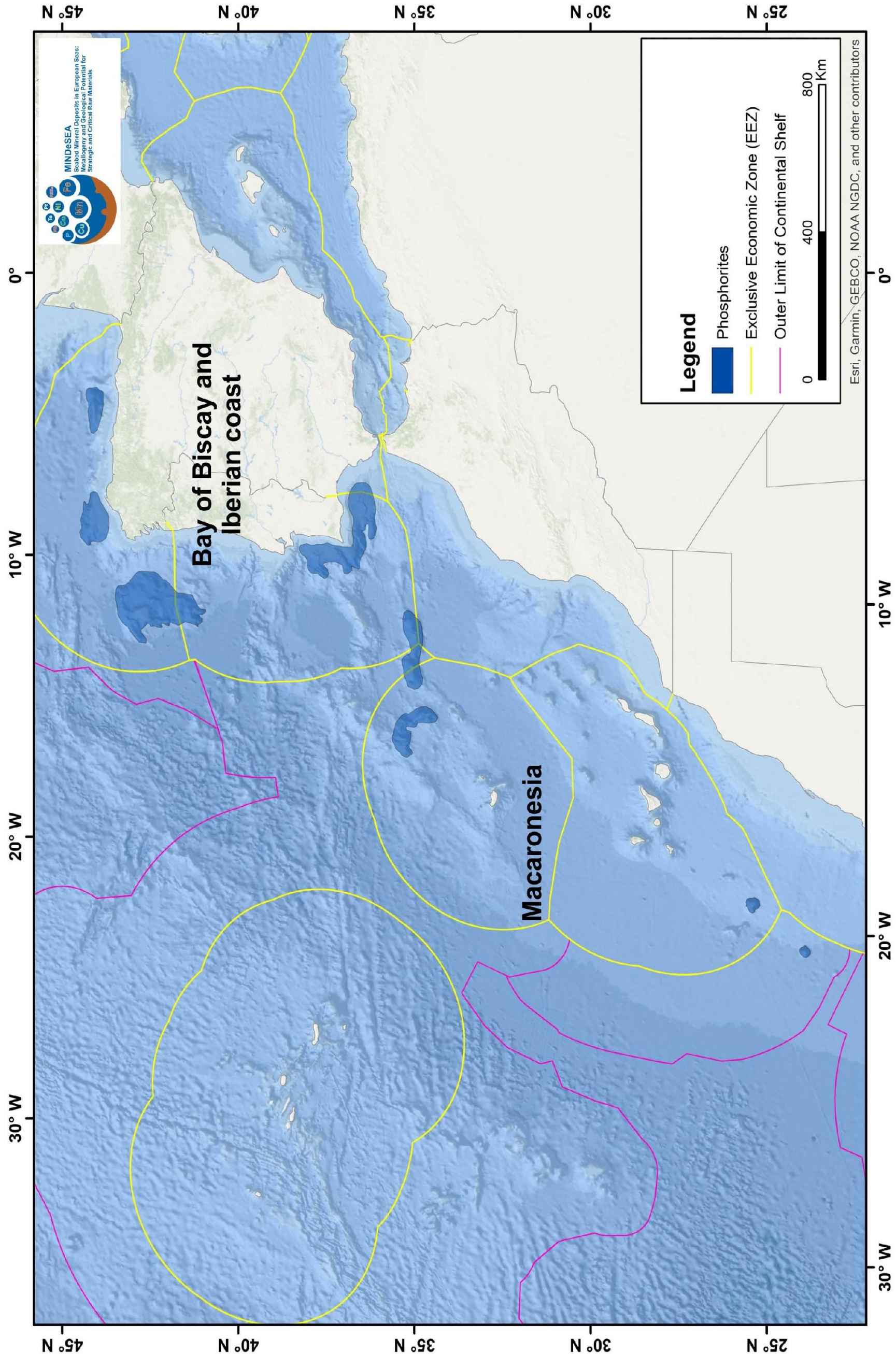
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Metallogenic provinces for ferromanganese crusts defined in pan-European seas.



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Pan-European map of seabed phosphorites enriched in CRM. MINDeSEA dataset and cartography compilation.



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Metallogenic provinces for phosphorites defined in pan-European seas.