MINDeSEA

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

Deliverable 4.5: Exploration potential of CRM associated with submarine ferromanganese crusts and phosphorites in Europe

WP1 leader: **Geological Survey of Spain (IGME) - Spain**		
Instituto Geológico y Minero de España	**Address:** C/ Ríos Rosas, 23 28003 Madrid Spain	**Telephone:** +34 91 349 58 64 (F.J. González) **Email:** fj.gonzalez@igme.es
WP4 IGME: Dr. Javier González (WP Leader)		

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D.4.5. Exploration potential of CRM associated with submarine ferromanganese crusts and phosphorites in Europe

Summary:

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

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

This document reports the research and compilation works produced by the MINDeSEA partners, led by the Geological Survey of Spain (IGME-Spain). A brief introduction to the European Green Deal, Blue Economy and Critical Raw Materials (CRMs) is presented as priority actions of the European Commission for sustainable development of our Society. Critical and strategic minerals are defined and their daily common uses are presented in the second section. Finally, using our MINDeSEA dataset, we present an analysis of CRMs potential of ferromanganese crusts and phosphorites in pan-European seas based on environmental and geological features of the European seas; and proposing a selection of the most important strategic and critical metals associated with the different deposit types.

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1 INTRODUCTION

1.1 Critical Raw Materials

Critical Raw Materials (CRMs) are a group of elements that are economical and strategical important for the technology industry and economy of Europe. Their importance is growing faster due to their uses in several environmental technologies (wind turbine, solar panels), high tech industry (LCDs, touchscreens, smartphones, etc.) but also health, defence and space exploration (several alloys with different uses).

In this way European Commission has redacted the actualized list of CRMs in 2020 (Critical raw materials | Internal Market, Industry, Entrepreneurship and SMEs (europa.eu)) that comprises 30 elements and materials (**Fig. 1**) that are crucial for the European circular economy (European Commission, 2020a) and that were previously presented in the deliverable D4.4 (González et al., 2021).

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 1. EC 2020 Critical Raw Materials List.

European industries are mostly dependant of these elements from other countries export this is why European Commission previously sponsored the search of CRMs within European limits with several projects linked to the H2020 objective and actually that the Raw Material Information System (https://rmis.jrc.ec.europa.eu/) is developed the goal is to reinforce it. Even more European Commission is developing a plan for the CRMs scenario supply use and demand for the strategic sector and reviewing the list by 2023 with the latest knowledge.

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All of these actions are being implemented with the objective of reaching a digital and climate-neutral economy by 2050, in this way Europe is also focused on the geo-political aspect in order to anticipate future needs (European commission, 2020b)

The EU will contribute to global efforts towards better resource management in co-operation with relevant international organisations.

This knowledge base should enable strategic planning and foresight, reflecting the EU's objective of a digital and climate-neutral economy by 2050 and enhance its leverage on the world stage (**Fig. 2**). The geopolitical aspect should also play an integral part in foresight, enabling Europe to anticipate and address future needs especially for electric vehicle batteries and energy storage (Li and Co) and REEs. It is calculated that EU will need 18 times more lithium and 5 time more cobalt by 2030 and these amount will increase more by 2050, on the other hand REEs are essential in permanent magnets both for the electric vehicles but also for energy creation in wind generators and their demand will constantly increase by 2050 (Alves Dias et al., 2018; Bobba et al., 2020; European Commission, 2020b).

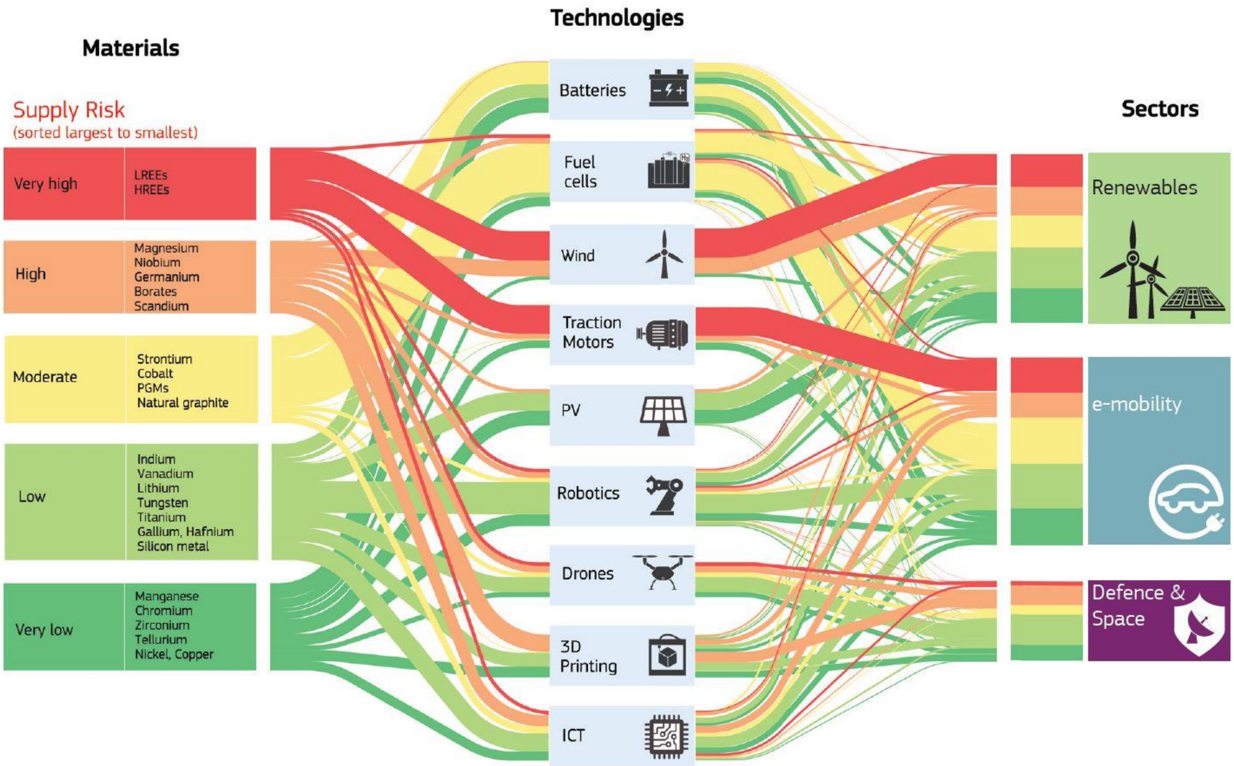

Figure 2. Schematic presentation of different CRMs and their uses in high tech and defence industry (Bobba et al., 2020).

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1.2 European Green Deal and Blue Economy

The European Green Deal (A European Green Deal | European Commission (europa.eu)) is the response of the European Commission to tackling climate and environmental-related challenges (European Commission, 2019). This is a unique opportunity to create a new EU in which the economy is not based on the resource exploitation and in which there are no net emissions of greenhouse gases in 2050. The proposal also aims to protect the health and well-being of citizen from environmental risk and pay attention to regions and workers that face the greatest challenge to reach it (**Fig. 3**).

Figure 3. The European Green Deal action and objectives (European Commission 2019).

The European Green Deal is also based on the concept that Europe has the collective ability to transform its economy and society in order to reach a sustainable path and became leader on climate measures. In this way is fundamental a public inversion in order to guide also the private capitals through environmental actions. It is a growth strategy for Europe.

The European Green Deal has two main objectives: boost the efficient use of resources promoting a circular economy; restore biodiversity and cut pollution, to reach the climate neutrality by 2050. Making Europe climate-neutral and defending our natural habitats will be good for society, planet and economy. No one will be left behind. To reach these objective is required to develop a series of action in all the sectors of the European economy including investments in environmentally friendly technologies, support industry to promote their innovation, find cleaner and cheaper form of private and public transport, encourage the decarbonisation of the energy and make energy efficient buildings, and finally work with international partners to improve global environmental standards. The Green Deal intends to finance the inclusive transition to a sustainable economy and that none of the countries have to be leaved behind, providing a secure and healthy planet for future generations.

Furthermore, European Green Deal is also supported by other initiatives as the EU Blue Economy (https://ec.europa.eu/oceans-and-fisheries/ocean/blue-economy_es). The Blue Economy includes all those activities that are marine-based or marine-related (**Fig. 4**). The Blue Economy established sectors include Marine living resources, Marine non-living resources, Marine Renewable energy, Port activities, Shipbuilding and repair, Maritime transport and Coastal tourism. Its objectives should help to achieve the Green Deal objectives and secure other complements linked to the marine environment as the mitigation of the climate changes with the development of offshore renewable energy and decarbonizing marine transports, promote a circular economy for fishing and recycle of ships, preserve biodiversity and coastal economy and developing green infrastructure in coastal areas.

The Blue Economy emerging and innovative sectors comprise marine renewable energy (i.e. Ocean energy, floating windfarms and solar energy and offshore hydrogen generation), Blue bioeconomy and biotechnology, Marine minerals, Desalination, Maritime defense, security and surveillance, Research and Education and Infrastructure and maritime works (submarine cables, robotics). These sectors offer significant potential for economic growth, sustainability transition, as well as employment creation. The Blue Economy supports the exploration and possible exploitation of marine mineral resources focused on the preservation and protection of the marine environment; where research, infrastructure and technological developments will be essential supporting tools (European Commission, 2021).

Figure 4. The European Blue Economy activities.

2 STRATEGIC AND CRITICAL ELEMENTS, DEFINITION AND USES

2.1 Strategic and critical elements

Metals and minerals are part of our daily lives. Nevertheless, large quantities are necessary for the modern society development, and no-country is full self-sufficient. Countries determine the list of minerals necessary for the growth of their economies in basis of the mineral policies or strategies like occur with the CRM List in Europe (European Commission, 2020a). Strategic and critical elements will change with time. Strategic elements are all of those elements, metallic or not, that

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are usually defined as vital to modern technology, defense and industry and that have a high economic importance. They are required for technological and industrial developments, but are in short supply and have no known substitutes. Between them is possible to classify several base metals like Fe, Mn, Cu, Ni and Zn. These elements have been listed here because, even if they are relatively abundant and largely exploited all around the world, their economic importance is increasing fast due to their common use and the growing of several new economies (China, India, Brazil, etc.) that demand great quantities of all these elements. Their uses are linked essentially to create different resistant alloys, electric cables and superconductors. Other strategic metals known as "precious" metals, like Ag and Au, are vital to both technology and industry and they are commonly by-products from base metal refining (**Fig. 5**).

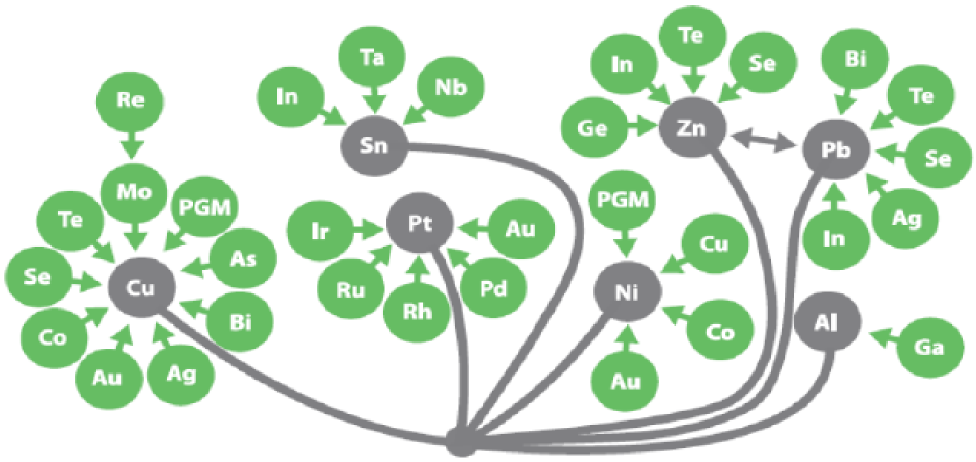

Figure 5. Sources of certain critical (and non-critical) raw materials (green) and their associated base metal (grey) (European Commission, 2018).

No standard methodology and classification have been stablished for selecting critical raw materials. There are different definitions and classifications with some common elements. The EU approach identifies critical elements or raw materials (**Fig. 6**) under the criterion of supply disruption risk and economic importance (European Commission, 2020a). The criteria in USA are risk of supply disruption, production growth rate and market development rate (Fortier et al., 2018; Nassar and Fortier, 2021). In the United States a The Energy Act of 2020 defines “critical minerals” as the minerals, elements, substances, or materials that “(i) are essential to the economic or national security of the United States; (ii) the supply chain of which is vulnerable to disruptions (including restrictions associated with foreign political risk, abrupt demand growth, military conflict, violent unrest, anti-competitive or protectionist behaviors, and other risks throughout the supply chain); and (iii) serve an essential function in the manufacturing of a product (including energy technology-, defense-, currency-, agriculture-, consumer electronics-, and healthcare-related applications), the absence of which would have significant consequences for the economic or national security of the United States" (Nassar and Fortier, 2021).

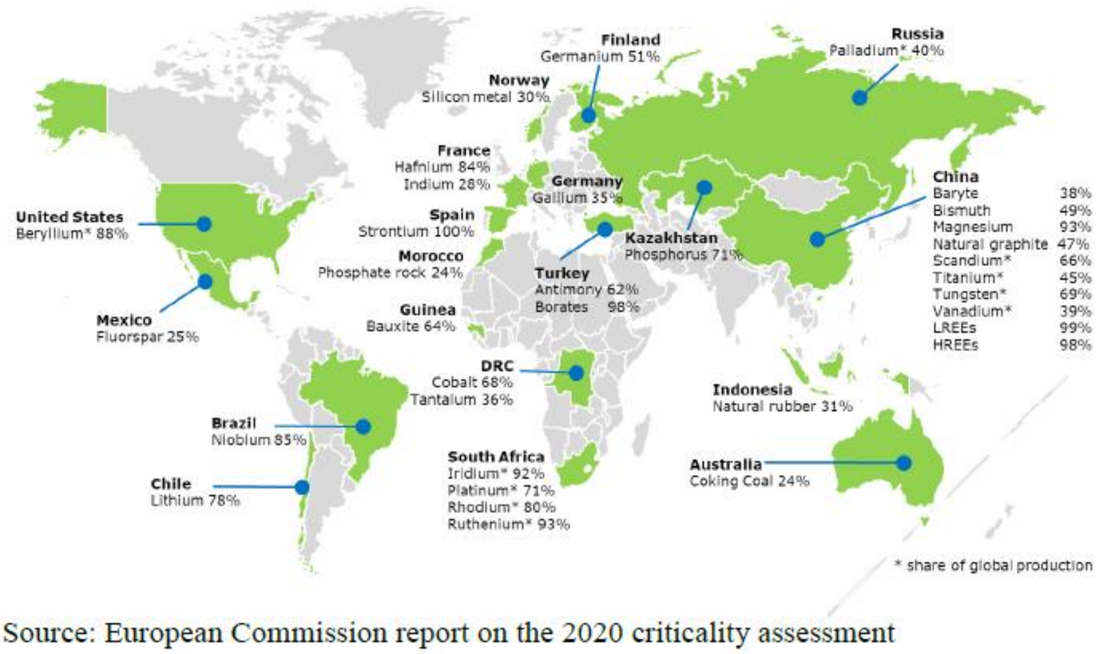

Figure 6. Biggest supplier countries of CRMs to the EU (European Commission, 2020a).

2.2 Energy critical elements

The term "energy-critical elements" (ECEs) was created by a joint committee of the American Physical Society and Materials Research Society assembled in 2009 to investigate the material resources available to support emerging energy technologies (Jaffe et al., 2011). In this group are reunited several elements which properties are related to the energetic potential both for the energy production (inductors, super magnets, solar cells, etc.), for the energy distribution (superconductors) or storage (high performance batteries) (Jaffe et al., 2011; Hein et al., 2013). Most of the ECEs have not been widely exploited, traded, or utilized in the past, and are therefore not the focus of well-established and relatively stable markets.

2.2.1 Photovoltaic elements

Photovoltaic elements group is represented by those elements (Ga, Ge, Se, In and Te) that are used in the creation of high sensitive and, especially, thin photovoltaic solar cells (Bobba et al., 2020). These elements also have other important uses: Te is employed in the creation of acid resistant

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super alloys, semiconductors or as a catalyst in oil refining; Ge is used in alloys as transistor in electronic applications, to create wide angle lens for cameras and microscopes; Ga is a silicon substitute in electronic industry, in LEDs lamps and to create low-melting alloys; Other uses of Se are its addiction in several glasses to reduce sunlight transmission, in pigments and ceramics to create stainless steel; finally, In , in his form as indium tin oxide, is an important element in touch and flat screens, indium nitrides are semiconductor and are used in microchips and In alloys are used in fire-sprinkles due to its low melting point (RSC, 2021).

2.2.2 Platinum group elements

Platinum group elements (PGEs) are represented by six elements (Ru, Rh, Pa, Os, Ir and Pt) in which Pt is usually the most abundant. These elements are useful for the fabrication of several conductive alloys and electronics components for the high technologies. Other uses are linked to the jewellery (essentially Pt) but also in the creation of surgical alloys, several of these elements are used in catalytic converters to reduce toxic gases emissions, in the catalysis of the oil to produce high refined gasoline and in several integrated circuits (Bobba et al., 2020; RSC, 2021).

2.2.3 Rare Earth Elements

In the group of the Rare Earth Elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb and Lu), that also includes Sc and Y, there are several of them that have energetic properties and uses. Most of the REY (Pr, Nd, Sm, and Dy) are used for the creation of high potential permanent magnets that are stronger per unit weight than other magnets. These magnets are used in wind turbine but also have several high-tech uses as in smartphones, tablets and Pc. Most of the REY, due to their chemical properties, are used in high conductive alloys but also in the glass industry in for cameras and smartphones. Between the others uses, REEs are essentially in super alloys, petroleum catalysts, batteries, LCD screens, LEDs lights, etc (Bobba et al., 2020; RSC, 2021).

2.2.4 Other energy critical elements

Other elements included in the list of the Energy critical elements are He, Li, Co, Ag and Re. Co and Li are actually used in high performance batteries for electric vehicles (EVs) and also Co is used in super-alloys. He, due to its unreactive behaviour, is used as cooler in the Large Hadron Collider (LHC), and the superconducting magnets in MRI scanners and NMR spectrometers, Re is used in Mo-W-Re alloys to make filaments in several technologies as X-Ray machines, Ag, finally, is used to

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make several alloys, electric contacts, batteries and as Ag paint in printed circuits (Bobba et al., 2020; RSC, 2021).

2.3 Other critical metals

Other critical elements listed in the European CRM List (European Commission, 2020a) are tungsten (W), antimony (Sb), vanadium (V), niobium (Nb), phosphorous (P) and phosphate rock.

W is used in several alloys essentially for its high melting point to make temperature resistant metals used ad electrode for example in arc welding. Sb is used in technology industry to make semiconductor devices but also to create harder alloys of soft metals like Pb that are also used in batteries. V and Nb are also used in several alloys, V alloys are shock resistant and also due to its low neutron-absorbing properties these alloys are used in nuclear reactors, on the other hand, Nb alloys are interesting for their low temperature resistance and are used in jet engines and rockets, furthermore Nb also have superconductive properties and is used in superconductive magnets in particle accelerators and other devices. Finally, phosphorous have a lot of different uses, as compound of incendiary devices, in the production of steel, in detergents and glasses. By far, the largest use of phosphorous is for fertilisers in the form of ammonium phosphates (Bobba et al., 2020; RSC, 2021).

3 EXPLORATION POTENTIAL FOR Fe-Mn CRUSTS AND PHOSPHORITES IN EUROPEAN SEAS

Ferromanganese crusts and phosphorites can be found in all the oceans covering different substrates or paving the seafloor. Their presence is linked to several factors that determine also their size, genetic process and enrichment in the different CRM, previously presented in the deliverable D4.4 (González et al., 2021). Here after we will show the interpretative analysis of the most important exploration potential areas for crusts and phosphorites in pan-European seas attending to the morphotectonic environment, the development of the Oxygen Minimum Zone, the age of the seafloor substrate and the water depth. CRMs potential and predictive maps in pan-European seas will be provided in the deliverable *D4.5 Mineral-potential and prospectivity maps*.

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3.1 Morphotectonic environment

Fe-Mn crusts occurrences listed in the MINDeSEA database are linked to the substrate and their formation vary depending on the morphotectonic environment in which are formed that are represented essentially by: 1) seamounts and 2) banks. Samples of the MINDeSEA database are located on seamounts of the Macaronesia area and the Iberian coast, on ridges and seamounts located in the Northeast Atlantic Ocean and associated with the Mid Atlantic Ridge and in the Arctic Ocean associated to the shallows seas formed by Barents and White Seas.

Phosphorites occurrences listed in the MINDeSEA database can be found in three main morphotectonic structures: 1) continental shelf; 2) banks and 3) seamounts. All the samples listed in the MINDeSEA database have been recovered in the Iberian Margin, essentially in the Galicia Bank area and on the seamounts and continental shelf of the south of Portugal. The presence of phosphorites slabs was described in several seamounts of the Macaronesia area as The Echo and Tropic seamounts of the CISP or the Ampére and Lion seamounts in the Madeira-Tore Rise area.

Abyssal planes

In pan-European can be found several abyssal planes located essentially in the north-east Atlantic Ocean and in the Arctic in average depths between 3000 and 5000 m. These abyssal planes are: 1) Porcupine abyssal plane, located in the area between the north Iberian Peninsula, the west of France and Britain islands; 2) Iberian abyssal plane, located in the north west of the Iberian Peninsula, between the Galicia Band and the Estremadura Spur; 3) Tagus abyssal plane, located at the south of the Estremadura Spur and limited by the Madeira-Tore Rise; 4) Madeira Abyssal Plane and Canary Basin are located to the west of both archipelagos respectively. Finally, different basins reach similar depth as the Norway and Lofoten basins.

Due to several factors as their depth, sedimentation rate and unconsolidated substrate, abyssal planes usually show scarce presence of ferromanganese crusts and, in the case they are present, form thin patinas covering marine deep sediments. Crusts formed in abyssal planes are usually hydrogenetic.

Seafloor sediments enriched in phosphates and REY have been recently discovered in abyssal planes from the Pacific Ocean (Kato et al., 2011; Tanaka et al., 2020). These kind of deep-sea sediments are unexplored in the pan-European seas, then abyssal planes surrounding the Iberian

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Peninsula and the Macaronesia should be potential targets for future exploration of phosphate-REY-rich muds (**Fig. 7**).

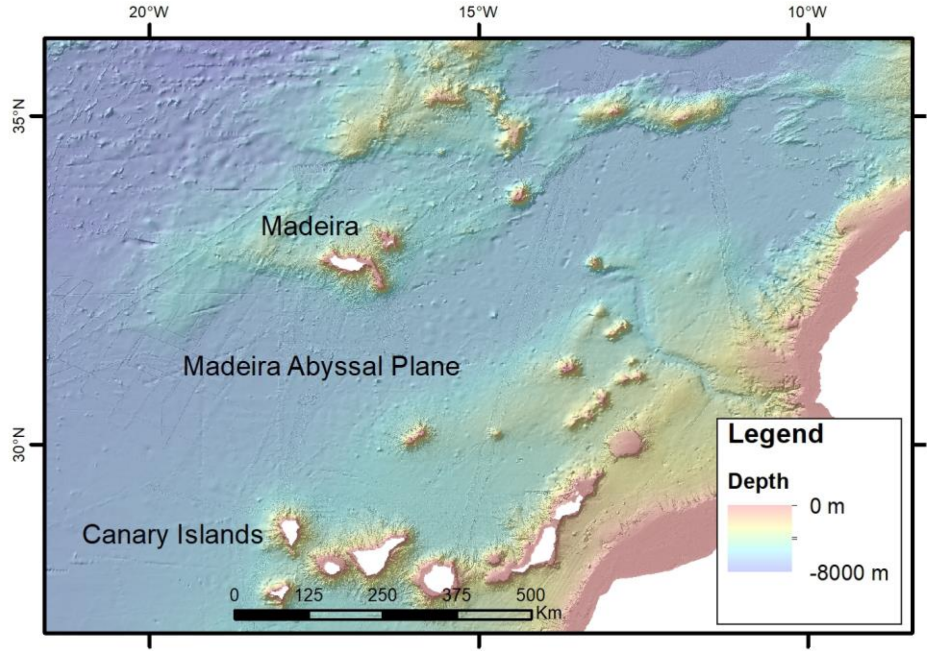

Figure 7. Bathymetric map of Madeira-Canary abyssal planes. They are potential areas for exploration of phosphate-REY-rich muds.

Ridges

Ridges can be divided as mid ocean ridges and fissure seamounts forming elongated chains and in European seas is possible to find both of these morphotectonic structures: 1) Mid Atlantic Ridge is part of the European domain essentially in the Azores and Iceland areas, but also in the Jan Mayen triple junction with an average depth of 2500 m in the submerged part; 2) ridge-like seamounts and chains can be find through all the European oceans as the El Hierro Ridge in Canary Islands (between 1000 and 2000 m depth), Jan Mayen ridge (100-900 m) or Aegir ridge in the Jan Mayen area (2000-3000 m), etc.

Ferromanganese crusts can be found covering slopes of ridge-like morphotectonic features but is possible to see several landslides marks that remark their cracking and fall during time, furthermore, due to their high steep flanks and morphology ridge-like deposits are not very suitable for economically easy Fe-Mn crusts exploitation. In Mid Oceanic Ridges Fe-Mn crusts usually have a clear dominant hydrothermal origin, with enrichments in Fe or Mn (depending on the vent fluids composition). These crusts usually form very rapidly and show growth rates varying between 100 and 1000 mm/Ma that promote the presence in active vents areas of very thick deposits (Hein et al., 2000). Due to this hydrothermal origin and their rapid growth these Fe-Mn crusts usually show low contents of strategic and critical elements, nevertheless occasionally they can contain important contents in some critical elements like lithium. Hydrothermal deposits are described in detail in the D3.4 deliverable of the MINDeSEA project (Schiellerup et al., 2021).

Banks and Plateaus

Banks and Plateaus are common in all the oceans and could be formed by fragments of Continental Crust separated from the main continents, for example Galicia Bank (800-1800 m) and Rockall Plateaus (200-1500 m), but also oceanic banks and plateaus formed by high volume of volcanic material as could be the Azores plateau. A part of these big banks and plateaus in European seas in possible to find several small ones, for example the Adventure Bank and the Malta Plateau in south west and south east of Sicily, or the Conception and Amanay banks.

Plateaus and banks form large flat areas in which is possible to accumulate high amounts of Fe-Mn crusts, many times associated with phosphorites (**Fig. 8**). The almost flat surface makes them suitable for exploiting these types of deposits. The formation of phosphorites in banks is linked to the presence flat areas in which the most important factor is the high productivity (upwelling) that allow accumulate great P contents in the waters that subsequently could precipitate due redox changes forming phosphorites slabs or replacements in previous formed carbonates and Fe-Mn crusts (González et al., 2016).

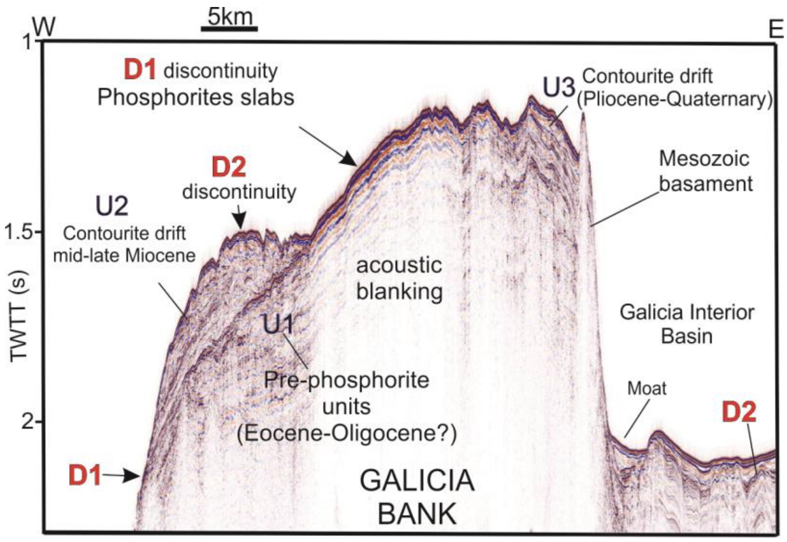

Figure 8. Multichannel seismic profile of the Galicia Bank and the sismo-stratigraphic position and sampling sites of Cenozoic phosphorite slabs (modified from González et al., 2016).

Seamounts

Seamounts can be found in all the European seas forming isolate submarine mountains or groups and chains. Seamounts have in general a volcanic origin, they can be differentiated from bank and ridges for they smaller extent both in longitude and area, moreover seamounts show a different geochemical signature that suggest different sources for different seamount chains (**Fig. 9A**) (Tetreault and Buiter, 2014). The higher amount of seamounts in pan-European seas can be localized in the Macaronesia area in which is possible to recognize hundreds of them as for example: 1) Tropic, Echo and The Paps seamounts in Canary Island Seamount Province (CISP); 2) Josephine, Tore and Nameless seamounts in the Madeira area; 3) Famous and Azores seamounts in the Azores islands area. Also they can be recognized near the Iberian coast as the Sancho or Descobridores seamounts located near the Galicia Bank and the south of Portugal respectively.

Seamounts accumulate large amounts of Fe-Mn crusts that usually forms pavements on their tops and slopes with thickness reaching up to 25 cm in some cases (Marino et al., 2017). In general seamounts present crusts with a hydrogenetic origin growing slowly through the time, in this way old seamounts could show great Fe-Mn deposits on their tops and slopes and be considered as interesting mine sites (Hein et al., 2009). Thick crusts on ancient seamount summits usually present internal replacements by phosphates, and occasionally substrates formed by phosphorite slabs (Hein et al., 2016; González et al., 2016). Examples of these kinds of deposits were observed in the Galicia Bank region and he Canary Island Seamount Province.

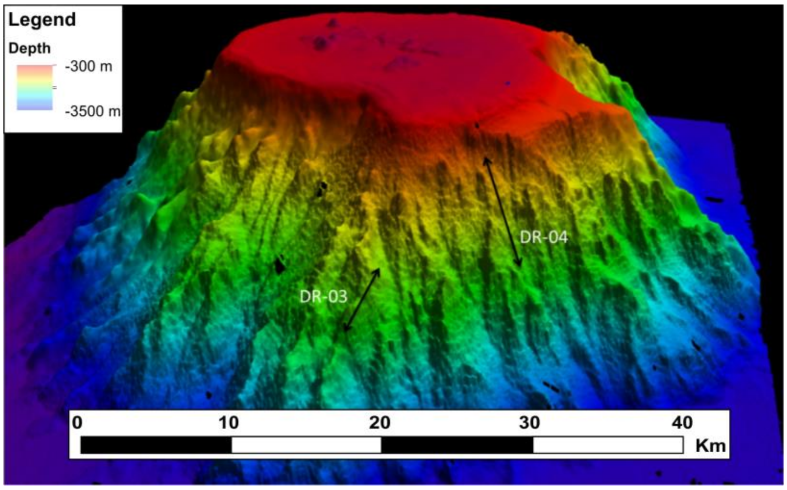

Figure 9. A) 3D bathymetric model representing the guyot-type Echo Seamount in the CISP with location of dredge stations (DR-03 and DR-04). Abundant pavements of ferromanganese crusts were recovered on the slopes. *DRAGO0511* Expedition.

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3.2 Oxygen Minimum Zone

The most important factor for the formation of Fe-Mn crusts with high contents of several strategic and critical elements is the presence of a thick Oxygen Minimum Zone (OMZ) in the area above the substrate in which Fe-Mn crust will grow. The development of a thick OMZ is also contributing to the phosphatization processes on seamounts and banks (González et al., 2016). In the OMZ is possible to find the presence of several important elements that forming Fe-Mn crusts and phosphates dissolved in their reduced state. Several authors demonstrated that a numbers of elements usually concentrated in the Fe-Mn crusts can be found enriched in the OMZ as is for some of the most important: Fe and Mn but also Co, Ce, Cu, Mo, Te, As, Pb and P (Koschinsky and Hein, 2003; Saager et al., 1997; Pohl et al., 2011).

When the Fe-Mn crusts are formed just below a thick OMZ crusts grow slowly because the elements, and especially Fe and Mn that form the main structure, remain dissolved in their reduced state. On the other hand, when the oxygen contents of the OMZ vary due to the presence of oxygen rich currents that promote a mix in the waters these elements precipitate (Hein et al., 1997; Marino et al., 2017).

In this way the presence of a thick OMZ is important for two main reasons: 1) concentrate several elements in the water that with time and the action of currents can be incorporated in the Fe-Mn crusts and phosphorites; 2) promote a very slow growth rate of Fe-Mn crusts that allow the incorporation of other important non redox sensitive elements as REY, Ni, PGE, etc. In general, ancient seamounts and banks are potentially more affected for changes in the development of the OMZ, being promising areas for exploration of crusts and phosphorites.

3.3 Water depth

The water depth of the substrate in which Fe-Mn crusts could be formed is also another important factor. Previous studies on Fe-Mn crusts from all around the world allow recognize that crusts usually form at depth ranges comprised between 400 and 7000 m and the thickest Fe-Mn crusts have been situated between 800 and 2500 m (Hein and Koschinsky, 2014).

Depth is important because can vary the elemental contents of the crusts in several ways, for example shallow substrates could be affected by higher detrital input (dust or river input) increasing aluminium silicates elements to the detriment of important elements as Co, PGE and REY as well as increasing the growth rate of these Fe-Mn crusts, preventing their enrichment of all the interesting and valuable metals. Moreover, shallow substrates could not develop the presence of a thick oxygen minimum zone, not being enough to concentrate interesting contents of all the important elements that can be concentrated in it. Reversely, shallow waters between 30 and 400 m are a favourable environment for the formation of phosphorites, even if phophogenetic events are well known occurred during the Cenozoic in all the oceans promoting precipitation of phosphorites on deep seamounts located between 1400 and 2700 m (Roonwal, 1986; Hein et al., 1993)

On the other hand, deeper substrates are a not very suitable for Fe-Mn crust neither. Studies made on deep water Fe-Mn crusts show that these crusts are usually highly enriched in Fe but with lower contents of Mn. In addition, several elements like Co and Ni decrease with the increase of depth while others as Cu increase with depth (Hein et al., 2017). Moreover, studied deep Fe-Mn crusts show high Fe/Mn values and fast growth rates that primarily suggest a hydrothermal origin but that usually are influenced by a high Fe availability in deep waters and an increase of sediment input probably due to the action of bottom currents (Hein et al., 2017; Marino, 2020).

3.4 Substrate age

Another important factor to take into account for the predictability and exploration potential of Fe-Mn crusts and phosphorites is the age of the substrate in which these deposits were formed. In this way, better areas are those in which oceanic crust is relatively old (Mesozoic substrates) and essentially far from the Mid Atlantic Ridge. Fe-Mn crusts with higher thickness and elemental contents have been reported to be more than 60 Ma old (Frank et al., 1999; Marino et al., 2018; 2019). Furthermore, several global phosphogenetic events are known promoting precipitation of thick phosphorite slabs in all the oceans. Two mayor global events have been dated between 20 and 40 Ma (Cenozoic) forming most of the phosphorites studied in the Pacific and Atlantic oceans (Hein et al., 1993; González et al., 2016).

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4 POTENCIAL CRM ASSOCIATED WITH Fe-Mn CRUSTS AND PHOSPHORITES IN EUROPEAN SEAS

Fe-Mn crusts and phosphorites concentrated high potential contents of several elements that have been recognized as strategic and critical by the European Commission (European Commission 2020a). The elemental contents of each element depend both to the mineral type and the different genetic process that formed each studied mineral deposit.

4.1 Strategic elements

Strategic elements can be found in Fe-Mn crusts both forming the main mineral structure (as Fe and Mn) as well as in secondary position sorbed on the minerals due to the presence of positive and negative free charges. Fe and Mn can reach an average content of 23 and 11 wt. % respectively in European Fe-Mn crusts (MINDeSEA, 2021). They appear as oxides and several studies suggest that they can be easily recovered with different metallurgical methods. Ti contents in Fe-Mn crusts are not very high but are anyway interesting (in average 0.7 wt. % and maximum of 2.4 wt. %). This element is usually associated to the Fe-oxyhydroxides entering in their structure or forming separated particles of Fe-oxides as magnetite/ilmenite.

Nickel is usually found in the interlayer formed by the hydrogenetic phillomanganates like vernadite and birnessite, but also in the tunnel structure and interlayer of diagenetic minerals as todorokite, asbolane and buserite (Hein et al., 1997; 2000; Post, 1999, Manceau et al., 2014; Marino et al., 2018; 2019). Copper could be found both sorbed on the structure of the Mn oxides, like Ni, and on the structure of the Fe oxyhydroxides due to the different oxidation states in which can be found dissolved in seawater (Donat et al., 1995; Koschinsky and Hein, 2003). Ni show an average content of 0.2 wt. % in Fe-Mn crusts from European seas with maximums of 0.9 wt. %, on the other hand, Cu has an average content of 0.1 wt. % and can reach maximum of 0.3 wt. % (MINDeSEA, 2021).

Both of these elements are commonly extracted worldwide but due to the improving of the quality life in several countries (Africa, China, India, etc.) their demand has been growing steadily and is important to take in account their presence in marine deposits.

Zinc and molybdenum are both important metals used essentially in the creation of different alloys resistant to rust and with a high conductivity, but also Zn is used as anti-corrosion agent and as anode in batteries while Mo have some application as pure element or isotope in medical

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technologies. Zn contents are mostly related to Mn minerals and essentially diagenetic minerals show the highest contents of this metal (Hein et al., 2000; Hein and Koschinsky, 2014; Marino et al., 2019). Mo on the other hand show similar contents both in diagenetic and in hydrogenetic minerals and is clearly linked to the Mn minerals (Mohwinkel et al., 2014; Marino et al., 2018; 2019). In European Fe-Mn crusts these elements have an average content of 550 and 250 µg/g respectively and maximums of 1000 and 450 µg/g (MINDeSEA, 2021).

4.2 Energy Critical Elements

All of these elements can be found in Fe-Mn crusts with different amounts. Co shows, between the trace elements, the highest contents in Fe-Mn crusts and is concentrated by direct oxidation directly on the Fe-Mn oxyhydroxides (Hein et al., 1997; 2000). Co can be found in all the genetic types of Fe-Mn crusts but the most enriched are the hydrogenetic with average contents of 0.5 wt. % in pan-European seas but reaching contents of up to 1 wt. % in punctual hydrogenetic minerals studied with high resolution analyses (**Fig. 9**). Diagenetic Fe-Mn crusts of pan-European seas are found essentially in the Barents and Kara seas in which Co contents are clearly low with an average of 200 µg/g. Finally, hydrothermal Fe-Mn crusts could show different contents of Co but will be described in the WP3 metallogenetic reports on hydrothermal mineralization (Schiellerup et al., 2021).

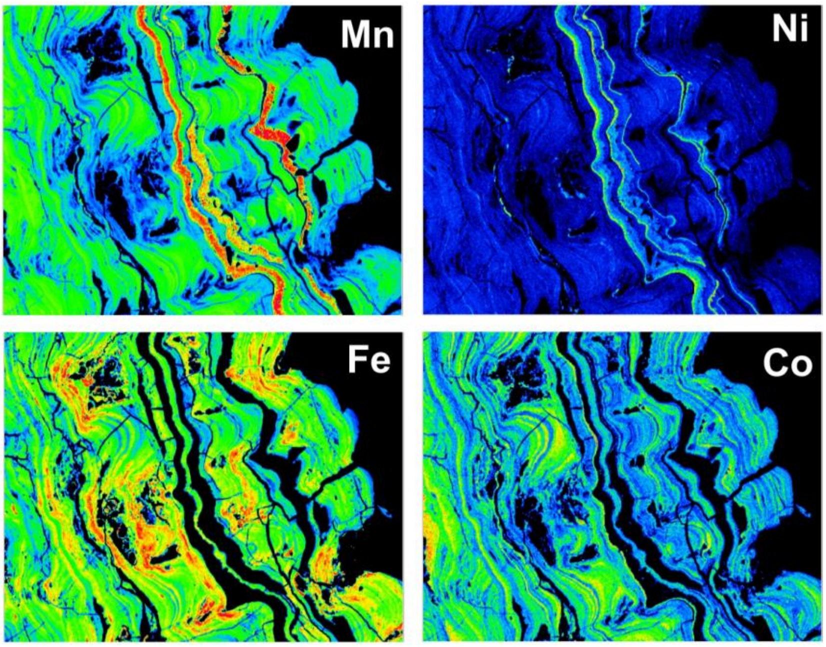

Figure 10. Electron probe microanalyzer (EPMA) strategic and CRMs mapping obtained on a thin section of a Fe-Mn crust (Marino, 2020).

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Te is the most enriched element, if compared with the Continental Crust, in hydrogenetic Fe-Mn crusts. This element can be found in several oxidation states in seawater and is specially enriched in Fe-Mn crusts that show lowest growth rates (1-6 mm/Ma). Several studies show that the purest hydrogenetic endmembers show contents ranging from 60 µg/g for bulk analysis up to 160 µg/g in punctual laminae; demonstrating the enrichment in crusts versus the continental crust of more than three order magnitude. On the other hand, diagenetic Fe-Mn crusts show no appreciable contents of Te (Hein et al., 2003; Marino et al., 2019). There is just 17 analyses of Te in MINDeSEA database, and all of them are localized in the Macaronesia area with average bulk contents of 36 µg/g and maximum of 70 µg/g.

Se contents in Fe-Mn crusts seems to not have any relationship with the hydrogenetic process and in general did not show high contents in Fe-Mn crusts, reaching just 1 µg/g in crusts worldwide (Takematsu et al., 1990). In MINDeSEA database there are no analyses of Se.

On the other hand, In, Ge and Ga are linked to the hydrothermal process and were described in detail in the deliverable D3.4 (Schiellerup et al., 2021).

PGEs are known to concentrate in hydrogenetic Fe-Mn crusts worldwide with contents between 200 and 700 ppb. Several authors have studied the processes that cause the enrichment of PGEs in Fe-Mn crusts, but this is still not clearly known. Some authors found that Pt and other PGEs are oxidised directly on the surface of the freshly precipitated Fe-Mn oxides and also they could be enriched in these samples by diagenetic and phosphogenetic processes (Hein et al., 2000; 2003; Koschinsky et al., 2005; 2019). In the MINDeSEA database PGEs values have been registered only in the Canary Islands seamounts with an average and maximum contents of respectively 245 and 330 ppb, while there was no analysis on phosphorites for PGEs contents.

REEs can be found both in Fe-Mn crusts and phosphorites but with some differences. In Fe-Mn crusts REY are enriched in hydrogenetic samples by slow incorporation of these elements through the time. REY elements can be found dissolved in seawaters forming both mono and di-carbonate or oxyhydroxides complexes that where sorbed on the charged surface of the Mn oxides and Fe oxyhydroxides (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003). LREE are the most enriched elements in Fe-Mn crusts and between them Ce is the most enriched with contents that are up to 2500 µg/g (Hein et al., 2000; Marino et al., 2017). In phosphorites REY elements, essentially Y and other HREE, are concentrated in francolite minerals in which enter substituting Ca (Jarvis et al., 1994; Piper, 1999; Emsbo et al., 2015).

REEs have been analysed in several samples of Fe-Mn crusts and phosphorites from the pan-European seas. In Fe-Mn crusts the total of REY has an average content of 0.2 wt. % and maximum of 0.3 wt. % in which Ce has contents of 1300 µg/g in average and 1800 µg/g of maximum. REEs in phosphorites only have been analyzed in four samples of the MINDeSEA database showing an average content of 0.1 wt. % and a maximum of 0.14 wt. %, Y is the most abundant element of the group reaching 420 µg/g.

Li, on the other hand, is mostly enriched in diagenetic deposits but the only analyses of Li in the Fe-Mn crusts database are high resolution analyses obtained in several laminae of Fe-Mn crusts from the Canary Island Seamount Province. In these analyses was clear that diagenetic laminae concentrated the highest amounts of Li, up to 900 µg/g, and an average content of 200 µg/g (Marino et al., 2019). In this work, hydrogenetic laminae were also analyzed showing low Li contents of an average of 40 µg/g and maximums of 100 µg/g. Is known that Li could be also enriched in Fe-Mn crusts with hydrothermal origin and its abundances are related to the contents of Mn and Fe in the crusts and their mineralogy and the Li concentrations in the parent fluids (Chan and Hein, 2007). In this way, hydrothermal Fe-Mn crusts could show different contents of Co and Li but will be described in the WP3 metallogenetic reports on hydrothermal mineralization: Li contents in hydrothermal Fe-Mn crusts (Schiellerup et al., 2021).

In the MINDeSEA ferromanganese database Ag, Re and He were not show in the analysis dataset. The global bibliography shows that the only element usually analyzed in Fe-Mn crusts is Ag showing usually contents below the detection limit (Hein et al., 2000).

In 2018 the MINDeSEA Consortium published ***First compilation map of "energy-critical elements" in pan-European seas: ferromanganese deposits***, based on data of the occurrence of submarine cobalt-and lithium-rich ferromanganese deposits (**Fig. 11**). The map, updated in 2019, shows the resource potential for these "energy-critical elements" in nodules and crusts (González et al., 2019). This map and the associated dataset showing the distribution of occurrences for both commodities in the European marine regions, has been included in the EU Blue Economy Report 2021 (European Commission, 2021).

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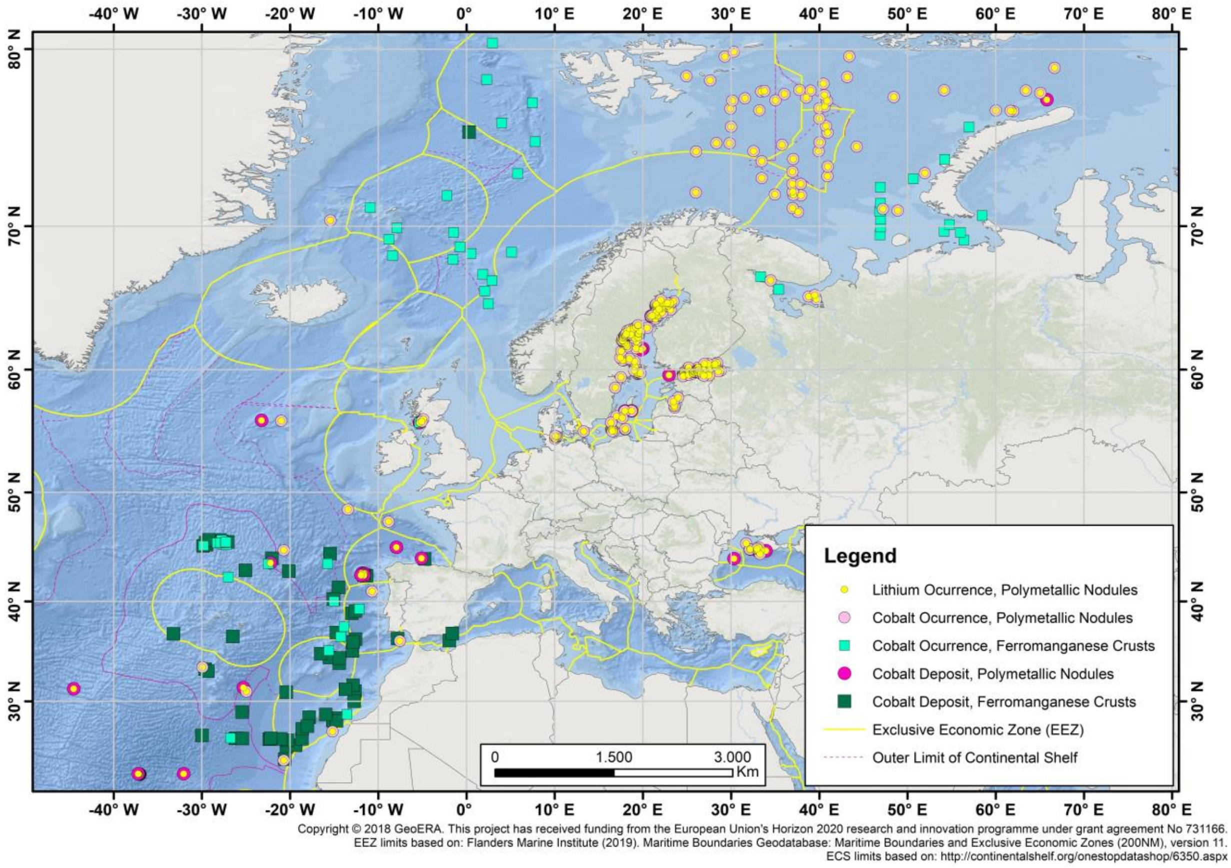

Figure 11. Distribution of occurrences of Cobalt and Lithium in pan-European seas: ferromanganese deposits, status per 20.12.2019 (González et al., 2019). Extended Continental Shelfs are presented in the map as submissions to the CLCS (Commission on the Limits of the Continental Shelf, United Nations).

4.3 Other critical metals

In Fe-Mn crusts is possible to find W, Sb, V and Nb with contents that are high compared to the Continental Crust especially in Fe-Mn crusts with a hydrogenetic process and associated both to the Mn oxides or the Fe oxyhydroxides, with average contents of 100, 40, 700 and 50 µg/g (Hein et al., 2000; Marino et al., 2018). In pan-European seas there are not Sb analyses for ferromanganese crusts, but the other elements show the average contents of these elements of respectively 73 (W), 600 (V) and 32 (Nb) (MINDeSEA, 2021). Ferromanganese crusts also could show interesting contents of P if they have suffered phosphatization with punctual values of up to 2.5 wt. %.

Phosphorous, on the other hand, is highly enriched in phosphorites and in pan-European seas can be found with contents varying from 8 to 12 wt. %. P is accumulated due to the decomposition of organic matter in bottom waters of upwelling areas in which the great productivity also generates a

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suboxic to anoxic environment (**Fig. 12**). Phosphorites are formed by authigenic precipitation of new formed phosphates in periods in which the water redox condition varies, or substituting and replacing previous precipited minerals like carbonates or Fe-Mn crusts (McCellan and Gremillion 1980; Hein et al., 2000; Kudrass et al., 2017).

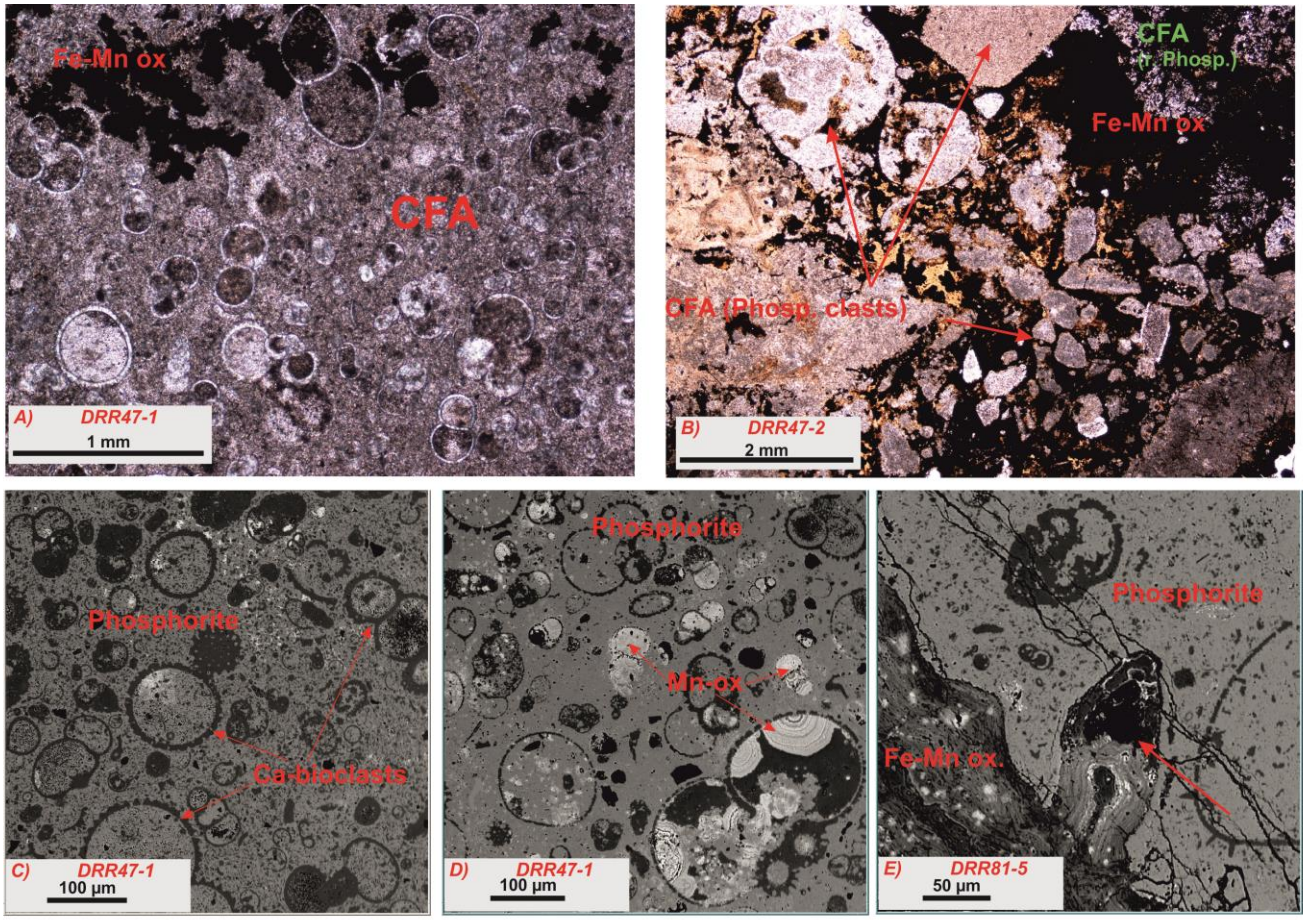

Figure 12. A, B) Petrographic microscope and EPMA images (C-E) of phosphorites from Galicia Bank in which is possible to identify bioclasts, phosphorite replacement of carbonate cements and clasts and Fe-Mn oxides (Modified from González et al., 2016).

4.4 CRMs exploration potential by marine region

According to the data collected in the MINDeSEA database is possible to establish potential exploration areas in pan-European seas linked to the different CRMs, the mineral deposits and the morphotectonic environment that are present in each of them.

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4.4.1 Macaronesia

The Macaronesia area is formed by a great number of volcanic islands and specially hundreds of seamounts located at water depths between 200 and 5000 m that can host thick pavements of Fe-Mn crusts (up to 25 cm). Furthermore, in the area is present a thick OMZ due to the high productivity promoted by the presence of upwelling currents that bring nutrients to shallow waters, that promote slow growth rates of Fe-Mn crusts and also the presence of phosphorites slabs at the base of the crusts (Marino et al., 2017). In this area the potential exploration is focused on the presence of hydrogenetic Fe-Mn crusts and all of those elements enriched in this type deposit. In the MINDeSEA database there are several indications of Fe-Mn crusts presence (CISP, Madeira-Tore rise) but there are large unexplored areas full of suitable seamounts that have a high predictability and exploration potential as could be the area of the Gran Meteor seamount or several of the unstudied seamounts that form the Tore rise. Macaronesia deposits are especially interesting for their high contents of several critical elements as Co, REE, Te (reaching contents of 0.6, 0.4 wt. % and 80 ng/g) but also great content of strategic elements like Mn, Ni and Mo (in average 18, 0.2 wt. % and 400 ng/g).

The area has also potential for exploration of phosphorites that could be found most of the times at the base of the Fe-Mn crusts or paving the summit of guyots.

4.4.2 Northeast Atlantic Ocean

MINDeSEA database report the presence of several deposits located in this area linked both to seamounts and ridge-like substrates. Bathymetric studies show that in this region there are hundreds of potential sites for the accumulation of interesting deposits of Fe-Mn crusts. In the area of the Norwegian there are several indications of this potential (MINDeSEA, 2021). One interesting area in this region is represented by the Jan Mayen in which are present banks, plateaus, ridges and seamounts. The area is affected for some hydrothermal input but is suitable for the presence of Fe-Mn crusts with mixed origin (hydrogenetic-hydrothermal).

4.4.3 Arctic Ocean

In the MINDeSEA database, samples belonging to the Arctic Ocean are located essentially in the Barents and Kara seas. These areas are not very suitable for the presence of interesting Fe-Mn crusts deposits, due to their shallow waters and the absence of hard surfaces formed by banks and seamounts, even if there are several indication of the presence of Fe- rich diagenetic crusts with

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low contents of CRMs (MINDeSEA, 2021). In any case, the Arctic Ocean, especially the deep area in the north of the Atlantic Ocean, is candidate as predictability and exploration potential area due to the indication of Fe-Mn crust discovered and studied in the Far East Arctic Ocean. These crusts were studied reporting interesting contents of different critical elements as Co, REEs etc (Hein et al., 2017; Konstantinova et al., 2017).

4.4.4 Bay of Biscay and Iberian Coast

Finally, in the region located around the Bay of Biscay and the Iberian coast there are several areas that show a high exploration potential. The area located in the Galicia Bank present several indications of Fe-Mn crusts both in the main bank as well as in the seamounts located around it, moreover, the area located at the north of Galicia also show the presence of several seamounts located near the continental shelf border, in which have been also found Fe-Mn deposits (Ercilla et al., 2011; González et al., 2016). Fe-Mn crusts recovered on the Galicia Bank are highly enriched in Mn, Co and Ni, but show low REEs contents (respectively in average 21, 0.9, 0.7 and 0.17 wt. %).

This region also shows the presence of the most enriched phosphorites found in pan-European seas. These deposits are linked to the presence of banks, seamounts and the continental shelf. Phosphorites slabs found in the Galicia Bank, but also at the south of the Iberian Peninsula show the highest contents of P recovered in the MINDeSEA database with contents of up to 20 wt. % Other critical elements enriched are REE (up to 0.2 wt. %) and F (2.4 wt. %).

5 FINAL REMARKS

This report provides the basis of future research/exploration surveys related to the potential of CRMs in pan-European seas. This analysis is based on the bathymetric study of the sea floor of the European margins, to highlight the different morphotectonic features, and on the bibliographic mineralogical and geochemical data collected during the compilation of the MINDeSEA database. Furthermore, other factors have been also considered like the age of the substrate, the presence of the OMZ and the water depth.

In pan-European seas is possible to highlight several areas that have both predictability and CRM potential. The Macaronesia area show the highest potential for the presence of Fe-Mn crusts,

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essentially with a hydrogenetic origin, enriched in most of the critical, energy and strategic elements (Mn, Co, REEs, Te, Nb, Ti, V, Mo, PGEs, etc). Flat top Cretaceous seamounts with thick ferromanganese crusts, and occasionally phosphate replacements exhibit the most suitable characteristics for CRM potential (**Table 1**).

On the other hand, areas like the Northeast Atlantic Ocean and Arctic Ocean that have not been extensively explored show the highest predictability potential. Both marine regions show several morphotectonic features suitable for the presence of Fe-Mn crusts at water depths in the range of these deposit type. Preliminary studies on some occurrence indicate this potential.

Fe-Mn crusts are important due to their contents of several CRMs and other strategic elements. Depending on the genetic process these deposits can concentrate high contents of Co, Ni, Te, Ti, Nb, REEs, etc (hydrogenetically formed) or, on the other hand, high contents of Mn, Ni, Cu, Li, etc. (diagenetically or hydrothermally formed), presenting high CRMs potential (**Table 1**). Moreover, phosphorites are also important as phosphates rocks, with high contents of P, F and REEs (essentially HREEs and Y).

Table 1. Summary of the different group of elements and their exploration potential in Fe-Mn crusts or phosphorites. The most prominent features are marked in bold.

	Fe-Mn CRUSTS				**PHOSPHORITES**	
Technological uses	Energy Critical Elements	Strategic Elements	Photovoltaic Elements	Other Critical Elements	Energy Critical Elements	Other Critical Elements
Elements	**Co**, **REEs**, Li	**Mn**, **Fe**, **Ni**, Cu, Zn, Mo	**Te**, Se, Ge, Ga, In	**Ti**, **V**, **Nb**, W, Sb,	REEs (**Y**)	**P**, **phosphate rock**
Morphotectonic Environment	**Seamounts**, Banks and Ridges	**Seamounts**, Banks and Ridges	**Seamounts**, Banks and Ridges	**Seamounts**, Banks and Ridges	**Seamounts, Banks, Continental shelf**	**Seamounts, Banks, Continental shelf**
Water Depth (m)	800-2500	800-2500	800-2500	800-2500	200-2500	200-2500
Substrate Age	**Mesozoic**, Cenozoic	**Mesozoic**, Cenozoic	**Mesozoic**, Cenozoic	**Mesozoic**, Cenozoic	**Eocene-Miocene**, Quaternary	**Eocene-Miocene**, Quaternary
Genetic Process	**Hydrogenesis**	**Hydrogenesis**, diagénesis, hydrothermalism	**Hydrogenesis**, hydrothermalism	**Hydrogenesis**	**Authigenesis, diagenesis**	**Authigenesis, diagenesis**
Marine Sector	**Macaronesia**, Arctic Ocean	**Macaronesia**, Mid Atlantic Ridge	**Macaronesia**, Mid Atlantic Ridge	**Macaronesia**	**Bay of Biscay and Iberian coast, Macaronesia**	**Bay of Biscay and Iberian coast, Macaronesia**

Cobalt and Tellurium is an interesting tandem of energy-critical elements with high economic potential in ferromanganese crusts. Cobalt is found in the Earth's crust only in chemically combined form and is obtained as by-product in nickel, silver, lead and copper ores. Tellurium, obtained as by-product of copper minerals. The Democratic Republic of the Congo is the biggest cobalt producer in the copper belt area. In the European seas, cobalt occurs in ferromanganese crusts (up to 1%wt.)

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sequestered into the structure of iron-manganese oxy-hydroxides as well as large amounts of other strategic and critical elements like tellurium, nickel or vanadium. Numerous deposits of cobalt- and tellurium-rich ferromanganese crusts have been discovered and mapped, in seamounts and ridges the Macaronesia area (Portugal and Spain), being this area a potential target for further investigation and exploration. Other marine regions, like the Norwegian Sea or Arctic Ocean, should be explored in detail.

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