Review

Ocean-Floor Sediments as a Resource of Rare Earth Elements: An Overview of Recently Studied Sites

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Abstract: The rare earth elements (REE), comprising 15 elements of the lanthanum series (La-Lu) together with yttrium (Y) and scandium (Sc), have become of particular interest because of their use, for example, in modern communications, renewable energy generation, and the electrification of transport. However, the security of supply of REE is considered to be at risk due to the limited number of sources, with dependence largely on one supplier that produced approximately 63% of all REE in 2019. As a result, there is a growing need to diversify supply. This has resulted in the drive to seek new resources elsewhere, and particularly on the deep-ocean floor. Here, we give a summary of REE distribution in minerals, versatile applications, and an update of their economic value. We present the most typical onshore methods for the determination of REE and examine methods for their offshore exploration in near real time. The motivation for this comes from recent studies over the past decade that showed ΣREE concentrations as high as 22,000 ppm in ocean-floor sediments in the Pacific Ocean. The ocean-floor sediments are evaluated in terms of their potential as resources of REE, while the likely economic cost and environmental impacts of deep-sea mining these are also considered.

Keywords: rare earth elements (REE) geochemistry; economic value of REE; offshore exploration of REE; ocean-floor sediments; environmental impact of ocean-floor mining

1. Introduction

As developed economies across the world transition away from carbon-based fossil fuels, much of the alternative technology is dependent on an increasing number of relatively scarce yet critical elements. Rare earth elements (REE) belong to the group of critical elements, since they are vital to modern technologies. With the increased development of technology and the constant need for more advanced technical devices, the demand for rare earths is continuously growing worldwide. Considering the unique properties of REE, which can increase efficiency and performance in many technological products and techniques, they are safely considered as the key for a green energy future. REE are crucial components in many advanced technologies, such as electronics, medical and military applications, etc. [1–4]. The annual increase of REE consumption is variable, because it strongly depends on the discovery of new fields of REE application [5].

The leading industrialized countries (e.g., EU/Germany and Japan) established different rare earth strategies [4]. As a member of the EU, Germany has no strategy for sustainable REE supply. In general, the EU is strongly dependent on imports of strategically important raw materials and high-tech metals. However, until 2005, the European Commission (EC) did not fully realize that it had a critical dependency on REE. In 2007, a

"coherent political approach with regard to raw materials supplies" started to be discussed, but only in 2008 did the EC present the Raw Materials Initiative (RMI) [4]. On this initiative of 41 analyzed minerals and metals, it was found that 14 should be regarded as critical. From the beginning, the RMI was considered as neo-colonial, and the criticism created the situation that missing resource efficiency was the target [4]. Hence, in 2011, a strategy was adopted, updating raw materials with the main three pillars: fair supply from the world market, promotion of sustainable supply, and improved resource efficiency [4]. Finally, the European Rare Earths Competency Network suggested a strategy for the development of the European rare earths scheme, and it focused on opportunities for primary supply in Europe through resource efficiency and recycling [4]. The EU is trying to establish access to raw materials worldwide, but it is missing resource efficiency as a target. In comparison to the EU approach, the Japanese strategy is more sustainable. Although Japan is the third largest consumer of industrial metals, it is also a resource-poor country [4]. Since 2001, a recycling law was in force, and in 2012, Japan implemented the "Rare Earth Recycling Act". The electronic waste conversion described as "urban mining" permits the recycling of e-waste at a large scale. Nevertheless, typically only 1% of the REE are recycled from end products, while the rest is deported to waste [6].

In 2017, the EC prepared a report to highlight the importance of critical raw materials (CRM) for the more resource-efficient and more circular economy [7]. Light rare earth elements (LREE) and heavy rare earth elements (HREE) have been listed at the top of the CRM list, showing their supply risk at the maximum level [7]. The parameter "substitution index", described in the EC report as a measure of difficulty in substituting the material, was scored (for both economic importance and supply risk) with the maximum values between 0.9 and 1.0 for all REE.

China is the most influential country in terms of the global supply of the majority of CRM, i.e., rare earths [7]. Estimated mine production of REE from China accounted for approximately 84% of the global world production between 2011 and 2017, and ≈63% between 2018 and 2019 [8]. Among many deposits in China, only a few are of significant economic importance: LREE from the Himalayan Mianning-Dechang orogenic belt, Bayan Obo in Inner Mongolia, and most importantly, HREE from ion adsorption in clays in the southern part of the country [1,9–12]. Recently, China has reduced export quotas to combat environmental problems associated with REE mining and to cope with its growing internal demand [9,10]. Despite the fact that until the 1990s, the United States was the world's largest REE producer—the Mountain Pass mine (in SE California), in the late 1980s, China started mining terrestrial deposits and quickly gained control of global REE production [8]. Meanwhile, in 2002, the mining at the Mountain Pass deposit was stopped because of considerable leaching of radioactive by-products from the mine tailings (mainly Th and U) after the extraction of REE [11]. Thus, since 2009, China has been an effective monopoly producer of rare earths, despite the Mountain Pass mine resuming production between 2012 and 2015, making a total contribution of only about 4% of the world REE supply in that period [8]. This imposes increased global demands for REE and appropriate rare earth oxides (REO). An additional conflict with exportation strategy may appear because the actual bilateral scenario between the two world's biggest economies, China and the United States, is going toward radical changes. This fact together with the critical role of rare earths in high technology has triggered an urgent need for a better knowledge of the global natural resources of the REE [13]. Therefore, countries should re/start the REE mines to gradually reduce dependence on China's supply. To achieve this, not only land-based but also resources from the deep sea should be considered to meet demand for the years and decades to come [14]. World demand for REE has tripled in the last decade, and active exploration strategies for new resources can successfully substitute supply shortfall [9].

The resources of REE are concentrated in carbonatite-related deposits, alkaline igneous rocks, pegmatites, monazite and apatite veins, ion adsorption clays, and in some deep-ocean sediments [10]. In Figure 1, the global REO reserves worldwide estimated for 2019 [15] are presented by a statistical diagram. As expected, China remained the dominant

country with REE resources, with a total reserve equal to 44 Mt (39%) of corresponding oxides of rare earths. The reserves of Brazil and Vietnam follow, each with an estimated 22 Mt (each half of China, i.e., 20%). Russia is the fourth country with a resource of REO (around 12 Mt, corresponding to 11%), while India was estimated to have reserves of approximately 6.9 Mt (6%) of REO. Thus, as can be seen from the diagram, Europe and the United States need to develop the technical capabilities to assess and extract REE resources if they are to decrease their dependency on imports.
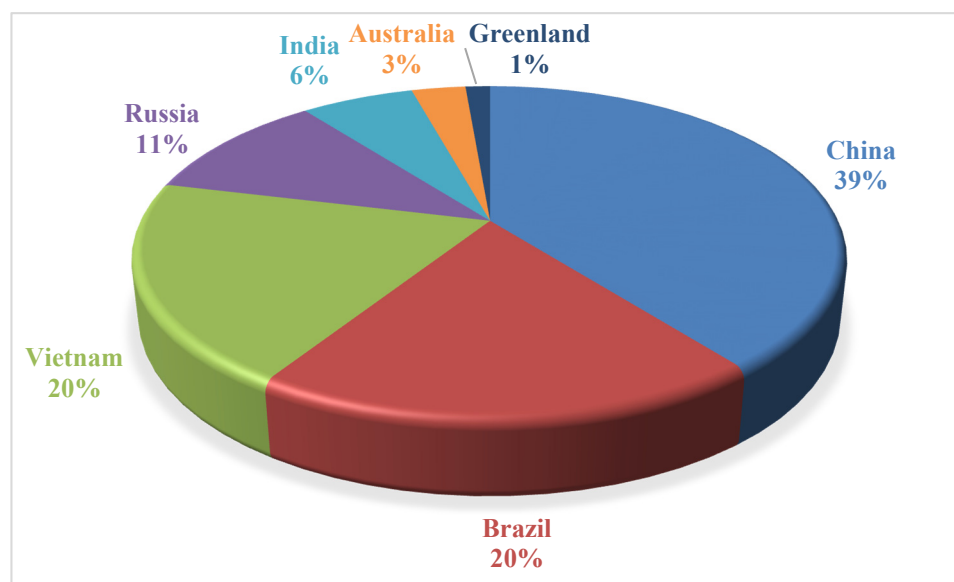

Figure 1. Rare earth oxides (REO) reserves worldwide; estimated statistical data for 2019 [15].

Compared to the global terrestrial (land-based) reserves, REO including Y and Sc can be in significantly higher amounts in the deep oceans, which is particularly known in the Indian and Pacific ocean bottom [2,16]. Notably, it is acknowledged that the two main terrestrial deposits have less than 1% of HREE, whereas in the Pacific cobalt-rich ferromanganese (Fe-Mn) crusts and polymetallic nodules, the amount of HREE can reach a level of as much as 26% [16]. Mining of the main minerals in Fe-Mn nodules and crusts from the bottom of the oceans can recover a very significant amount of REE as by-products [17]. In India, the principal ore mineral for LREE, monazite [(LREE)PO$_4$], is mined mainly in beach placers (70–75%), and the rest are mined in the inland and offshore areas [2]. Other REE minerals in India include ilmenite, sillimanite, garnet, zircon, and rutile, which are all dominantly containing LREE. In general, monazite and xenotime [Y,HREE(PO$_4$)] are two main potential resources for REE (LREE and HREE, respectively) that are present in a wide variety of rock types, but the concentration of extracted REE cannot support economies [18] because REE are typically dispersed; i.e., they are not concentrated in economically exploitable ore deposits. For mineral exploration and mining processes, of special interest is the detection of deposits (such as carbonatites, silico-carbonatites, peralkaline granites, pegmatites) enriched in REE. Although deep-sea mineral deposits, such as polymetallic nodules and cobalt-rich crusts, have been known for almost 50 years, only recent studies have indicated that unconsolidated ocean-floor sediments can also be good candidate resources for REE. So far, only a few investigations have focused on a quantitative assessment of the deep-sea floor for critical metal resources [19–27]. The estimations emphasize the importance of marine sediments and other classes of deposit (Fe-Mn crusts and polymetallic nodules) as promising alternative supplied for REE, compared with land-based resources [2,19]. Recently, there have been strong efforts to explore the potential supply of REE by cost-effective, low-carbon extraction and separation methods.

Within the EU, Portugal has a high area of jurisdiction (4127.408 km^2) and a very large ratio between the total areas of maritime zone and the continental shelf (M/C = 42.1);

thus, exploration strategies should be more focused on the res1ources available at the bottom of the Atlantic Ocean [28]. In addition to Portugal, several other European and non-European countries with significant areas of jurisdiction have similarly large M/C ratios and thus can explore their potential more. As an example, the United Kingdom (M/C = 28), New Zealand (M/C = 24.7), France (M/C = 16.9), and Japan (11.9) have also the possibilities to explore minerals and REE deposits in the deep-ocean floors. Several other countries have smaller ratios (M/C < 5), such as Chile (M/C = 4.9), Indonesia (M/C = 3.2), Australia (M/C = 1.4), and the USA (M/C = 1.2). The rest of the countries have a very small M/C ratio; i.e. M/C < 1. Unfortunately, to date, the sequences of mining of strategically important deposits of REE are poorly understood, and obviously, they are influenced by the mineralogy of the deposits [29]. The planning of the exploitation of REE deposits would benefit from a comprehensive mineralogical analysis [30]. The EU-FP7-funded project 'Blue Mining-Breakthrough solutions for sustainable deep-sea mining' produced much scientific and technical knowledge about the ocean-floor sediments, and it established standards for the best practices for the exploitation and economic use of mineral resources at the Trans-Atlantic Geotraverse (TAG) area in the Mid-Atlantic Ridge (MAR) [30,31].

In this review, the distribution of REE in minerals (as minor or major constituents), their increased importance, and their versatile applications in modern life have been summarized. An overview of the most typical onshore methods for the determination of REE are reviewed, as well as methods for offshore mineral and geochemical exploration (based on spectral data and statistical modeling of previously studied mining area), in near real time. The available recent research (i.e., studies performed in the past decade) on rare earth mineral resources in the global ocean floor unconsolidated sediments have been reviewed. Finally, the economic cost, environmental aspects, and future perspectives of ocean-floor mining have been commented on.

2. The Rare Earth Elements (REE)

2.1. The Chemistry of REE

The rare earth elements group includes the 15 lanthanides plus yttrium (Y) and scandium (Sc). REE are typically divided into two main groups, light (LREE), i.e., low-atomic number (Z) elements: lanthanum (La, Z = 57), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm, Z = 62), and heavy (HREE), with high-atomic numbers: europium (Eu, Z = 63), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu, Z = 71) [13]. Nevertheless, the classification is not consistent, and sometimes, the LREE group includes the group of La–Eu and the HREE group comprises the Gd–Lu series [18]. Moreover, the group of elements with mid-atomic numbers (from Sm to Ho) is named middle rare earth elements (MREE) [9,24]. The geochemical behavior of Y is similar to Ho, and hence, Y is included in HREE (average apparent Z = 66, based on its physical properties), forming a group designated as REY [32,33]. Yttrium is widely present in nature [18]. In addition to lanthanides and Y, Sc (Z = 21) is also considered as rare earth; however, it is sometimes excluded in the discussion of REE because it has a smaller cation with geochemical behavior closer to ferromagnesian transition elements, rather than REE [8,34,35].

The lanthanide elements have similar electronic configurations that set them apart from the rest of the elements. Namely, the REE have electrons in the 4f sub-shell, and this has a great influence on the oxidation state of these metals. Mostly, REE show an oxidation state of +3 (donate three electrons), except for the elements with oxidation state +2 (Eu) or the +4 oxidation state (Ce) (Table 1). The decrease in the size of atoms with increased nucleus charge generates small changes between their properties.

Table 1. List of the rare earth elements (REE), their relative abundances in the earth's crust (ppm), and main applications.

REE	Atomic Number (Z)	Oxidation State	Abundance * (ppm)	Applications ‡
Lanthanum (La)	57	+3	39	Camera lenses; catalysts for petroleum refining; MRI; new-generation electric vehicles; optical glass; rechargeable batteries
Cerium (Ce)	58	+3, +4	66.5	Catalyst for oil refineries; color screen, LCD; metal alloys; PET; polishing powder¸ radiation shielding; UV filters in glass
Praseodymium (Pr)	59	+3	9.2	Colorant in glasses; color screen LCD; cryogenic refrigerant; energy-efficient lighting; hard disk drives; lasers; magnets; pigments; portable electronics and small motors; radiotherapy techniques
Neodymium (Nd)	60	+3	41.5	Hard disk drives; new-generation electric vehicles; permanent magnets; portable electronics and small motors; treatment of skin cancers, violet colors in glass and ceramics
Promethium (Pm)	61	+3	trace †	Luminous paint; nuclear batteries
Samarium (Sm)	62	+3	7.05	Lasers; magnets; new-generation electric vehicles; Sm-153 treatment of tumors
Europium (Eu)	63	+3, +2	2	Bioimaging; color screen LCD; energy-efficient lighting; fluorescent lighting; lasers; portable electronics and small motors
Gadolinium (Gd)	64	+3	6.2	Lasers; magnetostrictive alloys; memory chips; MRI; neutron capture; steel additive
Terbium (Tb)	65	+3	1.2	Cancer therapies; color screen LCD; fuel cells; fluorescent lamps; high-powered electric motors; lasers; magnetostrictive alloys; optical computer memories
Dysprosium (Dy)	66	+3	5.2	Dy-165 treatment of effusions; high-powered electric motors; lasers; lighter vehicles; magnetostrictive alloys
Holmium (Ho)	67	+3	1.3	Cancer therapies; lasers; magnets; standards for optical spectrophotometers
Erbium (Er)	68	+3	3.5	Fiber-optic technology; lasers; medical and dental practice; steel
Thulium (Tm)	69	+3	0.52	Lasers; metal-halide lamps; Tm-167 in portable XRD-devices
Ytterbium (Yb)	70	+3	3.2	Chemical reducing agent; infrared lasers; stainless steel; Yb-176 medical application
Lutetium (Lu)	71	+3	0.8	Cancer therapies; catalyst; high-refractive-index glass; LED
Yttrium (Y)	39 (66.5) ‖	+3	33	Cancer therapies; ceramics; color screen LCD; compact fluorescent lamps; high-temperature superconductors; laser; LED; microwave filters
Scandium (Sc)	21	+3	22	Alloys for aerospace components; camera lighting; catalysts; color screen LCD; energy-efficient lighting; radioactive tracing agent in oil refineries; super alloys; X-ray tubes

* [36]; † [8]; ‡ [16,37,38]; ‖ apparent average atomic number (Z) based on physical properties of the element.

2.2. The Abundance and Applications of REE

Although they are described as "rare" earth elements, the abundance of rare earth elements in the earth's crust is not rare. They exist in nature from trace (negligible) abundances (Pm) to 66.5 ppm (Ce) (see Table 1). Promethium has no natural stable or long-lived radioactive isotopes but possesses around 40 short-lived isotopes [145]Pm [8]. On the other hand, Ce usually occurs in substitution to major elements in minerals, and as an example, it is more abundant than copper, Cu (50 ppm), in the earth's crust. The REE do not exist in free form in nature because of their high reactivity. Rather, they are major or minor constituents of minerals, such as silicates, carbonates, oxides, and phosphates [39]. The main economic sources of REE are bastnaesite [$(Ln,Y)(CO_3)F$], monazite [$(Ln,Th)PO_4$], and loparite [$(Ln,Na,Ca)(Ti,Nb)O_3$]. In total, there are about 250 minerals that contain rare earths [39]. The isolation of REE from minerals is a very complex procedure, including several steps, among which the most important are the extraction concentration, smelting, and refining. Thus, obtaining REE in pure metallic or oxide form from minerals makes them even more valuable.

The cellphones and other high-tech devices are composed of numerous metal components, many of which contain REE [1,4,16]. Namely, more than one-half of the components in cellphones (e.g., its electronics, display, battery, speakers, etc.) are made with a large involvement of REE [40]. According to statistical data, in 2019, about 1.52 billion units of smartphones were sold worldwide, and it is expected that it will increase in 2021 for 37% [41]. All REE (except radioactive Pm) can be found in varieties of smartphones, and some of them give colors to screens or vibrations (Dy and Nd) [42].

In the last three decades, the applications of REE have been extended in technological devices, such as computers, digital versatile discs (DVD), liquid-crystal displays (LCD), rechargeable batteries, autocatalytic converters, super magnets, light-emitting diode (LED) lighting, superconductors, glass additives, fluorescent materials, phosphate binding agents, etc. In the industry (electric vehicles, solar panels, wind turbines, etc.), the importance of REE is also very high. Some of the main applications of REE are listed in Table 1.

In addition to diverse applications in high-tech technologies, REE are also important in medical applications (e.g., medical diagnosis, anti-tumor agents, kidney dialysis medicine, surgical equipment, etc.) and medical instruments, e.g., magnetic resonance imaging (MRI), positron emission tomography (PET) imaging, and X-rays [38,43,44].

Some REE, such as Tb, Ho, Lu, and Y, have been considered as valuable elements in anticancer treatment because of their therapeutic radioisotopes, especially in radio-immunotherapy and photodynamic therapy [45]. Sm-153 and Yb-176 are also used in the treatment of tumors and in medical applications, respectively. Due to its superlative paramagnetic properties in the whole periodic table, gadolinium (Gd) is the most used rare earth in the MRI [29]. Gd^{3+} improves the contrast in magnetic resonance imaging scans with very low toxicity [46].

Since the REE are very important in all high-tech devices, and they are essential in modern medical applications in very low concentrations, these elements are often called "the vitamins of modern industry" [47].

2.3. Economic Value of REE

As previously stated, the extraction of REE from minerals is a very complex and time-consuming process. The cut-off grade in mining metallurgical operations is influenced by different economic indicators (e.g., market prices of both the primary product and the by-product, mining and processing costs, etc.). Moreover, the economic value of REE is multiplied due to their importance in numerous applications in modern technologies and globally constant growing tendency of the balance between demand and supply in the world market [48]. The separation and purification of individual REE is challenging due to their chemical similarities. In Figure 2, the current market prices of REO are presented according to the mineral price list [49]. The prices are shown per kg of each oxide of rare earth (high purity >99.5%) and as can be seen, they are in the broad range for all REO. As

an example, for some REO, the prices higher than 20,500 and 22,000 € (Er_2O_3 and Gd_2O_3, respectively), and 38,000 € and 41,600 € (Nd_2O_3 and Pr_2O_3), respectively. The remaining REO have lower values, e.g., around 1500 €/kg (CeO_2, La_2O_3, Sm_2O_3), 2600 €/kg (Y_2O_3), and from 240 to 540 €/kg for Dy_2O_3 and Tb_4O_7, can be noticed respectively. Currently, Eu_2O_3 and Sc_2O_3 (25 and 50 €/kg, respectively) are the rare earths with the lowest prices on the market.
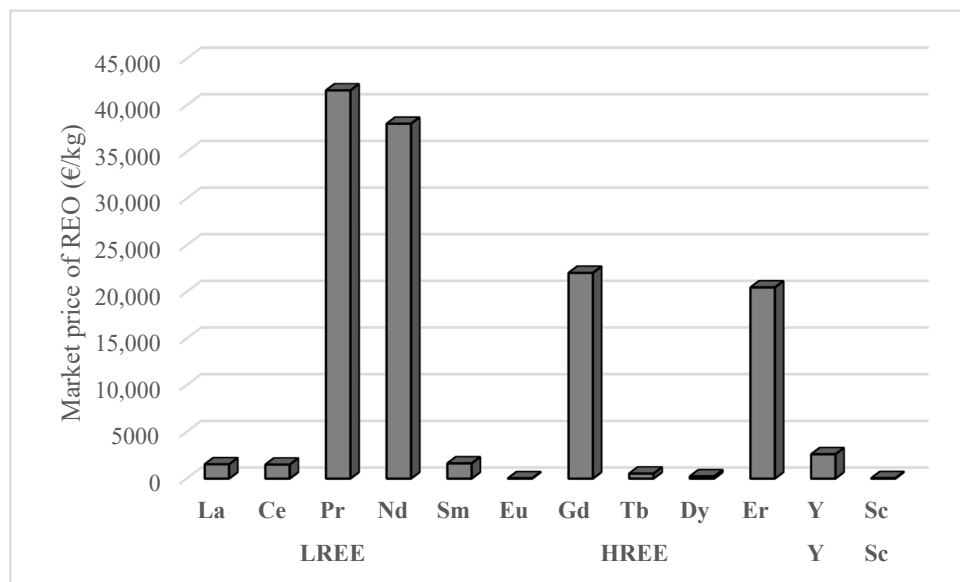

Figure 2. The actual market prices of rare earths: light rare earth elements (LREE) (La-Sm) + heavy rare earth elements (HREE) (Eu-Er) + Y + Sc. The prices (€) correspond to 1 kg of REO of high purity (>99.5%), updated in February 2020 [49].

3. Ocean-Floor Sediments as a Resource of REE

3.1. Onshore Methods vs. Offshore Exploration of REE in Ocean-Floor Sediments

The accurate analytical techniques for REE quantification are very important for their geochemical exploration, mining, extraction, and monitoring of the environment. With available instrumental techniques, several analytical methods are most commonly used for REE quantification, such as inductively coupled plasma coupled with optical emission spectroscopy (ICP-OES) or mass spectrometry (ICP-MS) detection. The ICP-based techniques are multi-element analytical methods used for the accurate and precise determination of REE at major, minor, and trace concentration levels in complex geological samples, such as sediments, crust samples, hard rocks, ores, etc. [2,50,51]. The ICP-methods are characterized with high sensitivity, covering a wide linear range of concentrations, with minimal interferences and high sample throughput. The techniques can simultaneously measure all rare earths at low concentration levels, after selecting the appropriate spectral lines [52]. ICP-MS is usually the method of choice for REE quantification in environmental and earth matrices because it has low detection limits with excellent sensitivity, of several orders of magnitude higher (10–100,000) in comparison with the ICP-OES method [50,51]. Therefore, the detection limits for the analysis of REE using ICP-MS are typically in ppb-levels ($\mu g \cdot kg^{-1}$ of dried material, e.g., sediment or rock sample). After using geological reference materials, it was shown that the limit of detection (LOD) for most of the REE can be even in ppt and sub-ppt ranges with a high precision, <5% relative standard deviation (RSD) [50]. Thus, ICP-MS methods are the best suited for high-precision geochemical studies.

In addition to ICP analyses, a technique such as X-ray fluorescence (XRF) can also be applied for the geochemical analysis as a reliable method for REE at the ppm level. The main advantages of XRF analysis are efficacy and cost [53]. Moreover, one of the main benefits of XRF is the possibility of using light, portable XRF devices for offshore quantification of REE (e.g., Ce, La, Nd, and Pr), which is of great importance for exploration

strategies during cruises, i.e., in near real time. Nevertheless, unlike the ICP-analyses, XRF is not REE-specific and has lower sensitivity, with an LOD at least two times less than the ICP-OES method [54]. Therefore, the XRF technique lacks sensitivity and is not suitable for the determination of REE at low concentrations, as is the case in most of the geological samples.

To explore the potential of conducting research at the bottom of the oceans (sediments, cover rocks, etc.), the research teams can apply two strategies: onshore methods and/or offshore exploration, depending on the mission objectives. In general, prior to analysis, after the careful sampling at the ocean bottom by drilling, TV grab, or gravity coring, collected samples can be stored appropriately in a nitrogen atmosphere (to prevent sulfide oxidation). Onshore analysis implies that after the mission is completed, the samples are transported into the conventional, full-fledged laboratories, where they can be pre-treated (e.g., dried) and treated (usually with a mixture of mineral acids in an automated high-temperature microwave digestion system). After digestion, cooled samples are typically transferred to decontaminated flasks and diluted before the running conventional ICP analyses. Thus, most of the available results are based on an onshore analysis in fully fledged laboratory conditions. The onshore identification of minerals is often postponed until long after the cruise is over. The main aim is to get a better knowledge of potential high-tech resources from deep-ocean sources; hence, these highly sensitive results can give insight into current perspectives.

On the other hand, offshore exploration of the collected samples from the bottom of the oceans can be applied synchronized during the mission. The extreme conditions on the cruise require specific technical set-up, which is entirely different from land-based analysis and pre-feasibility study. This type of fieldwork was performed under the Project Blue Mining—Breakthrough solutions for sustainable deep-sea mining, during the expedition of the M127 cruise, with recovered gravity cored sediments from the TAG hydrothermal field along the MAR [31]. Selected samples were analyzed for mineral composition by portable X-ray diffraction (XRD), and all on-board results were validated later, after the mission, by conventional, onshore XRD analysis. It was shown that mineralogy could be efficiently assessed during the cruises at sea; i.e., within 20 h, it was possible to analyze a batch of up to 24 gravity cored sediment samples [55].

Moreover, the rapid, non-destructive, and economically acceptable short-wave infrared reflectance (SWIR) spectral analysis could provide representative statistics for the offshore evaluation of geochemical variables in sediment samples from the deep ocean [55]. Thus, based on the previously established modeling equations, it is possible to substitute time-consuming destructive sample preparation (wet digestion and extraction) and conventional analytical methods (ICP-MS) by the portable infrared mineral analyzer (PIMA) using SWIR spectral analysis to get both qualitative and quantitative results of mineral components and geochemistry (e.g., La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, and Y) in previously studied ocean-floor areas, with high sensitivity. This new approach highlights the benefit of rapidly obtained spectral data that can be used for near real-time exploration of geochemical deposits in the ocean floor. This mode of work enables the modification of exploration strategies in light of new information as it becomes available in near real time.

3.2. The Concentration of REE in Ocean-Floor Sediments

The dominant resources of REE are available on the ocean floor [2,19,22]. Under aqueous conditions, REE exist mostly as a variety of complexes, with speciation dominated by metal, the predominant ionic form of some REE is trivalent $[REE]^{3+}$, carbonate $[REE(CO_3)]^+$, and di-carbonate $[REE(CO_3)_2]^-$, with carbonate complexes being the most abundant [8]. An increase in the pH of seawater leads to a preferable adsorption of LREE on suspended particles relative to HREE. The REE absolute concentrations in hydrothermal fluids are highly variable and can reach from a few to several thousand ppm by weight, and this enrichment is evident for LREE, in particular for Eu and Ce, which both exist in geological environments in two oxidation states (Eu^{2+}, Eu^{3+}; Ce^{3+}; Ce^{4+}) [8,24]. The

higher accumulation capacity of LREE relative to HREE in hydrothermal fluids can be explained by the higher stability of chloride and fluoride complexes with LREE [32]. In hydrothermal fluids, the REE composition is related to the interaction of oceanic crustal rocks with seawater at high temperatures [32]. Many ore deposits are more enriched with LREE than with HREE, and consequently, HREE became a more valuable commodity [9].

As previously mentioned, besides ocean-floor sediments, polymetallic nodules, cobalt-rich Fe-Mn crusts, and seafloor massive sulfides (SMS) are three other types of REE-rich resources in oceans. Polymetallic nodules occur in ocean-floor sediments at different water depths (of 1640–6500 m) in the oceans [56–59]. Cobalt-rich Fe-Mn crusts are composed of Fe oxyhydroxide and Mn oxide that precipitate from ocean water onto rock substrates [56]. The concentrations of REE in SMS are influenced by the REE patterns of the sulfide-forming fluids and interactions with subsea-floor rocks [60]. It was established that REE concentrations increase in deep water (from North Atlantic to North Pacific), and abundant REE are enriched in deep-sea sediments, which is mainly caused by the strong sorption capacity of sediments [61,62]. As an example, the concentrations of REE are 10–100 times higher in the deep-sea sediments compared to seawater [61]. Therefore, in this work, results are focused on unconsolidated deep ocean-floor sediments as potential REE-rich resources.

Conventionally obtained results by onshore ICP-MS analysis (performed after the wet digestion of homogenized and dried ocean-floor sediments samples) for the total concentration of REE (min–max range, expressed in ppm) are listed in Table 2. The results over the last decade show that large resources of REE (>1000 ppm) can be found in some ocean-floor locations (Pacific, Indian Ocean, etc.), which indicates that these highly valuable elements could be alternatively exploited at different deep-sea locations, thus diversifying the sources [19,21–23,33,53].

Table 2. Available data (2010–2020) on the total concentration of the REE in ocean-floor sediment samples worldwide.

Locality	Sediment Sample, Water Depth (m)	ΣREE, Min–Max (ppm)	Wet Digestion	Reference
Atlantic				
Main Lilliput, Roman City (9°32′–9°33′ S, 13°12′ W)	1486–1495	14.4–16.6	HF-HCl-HNO$_3$ aqua regia	[63]
Logatchev (14°45′ N, 44°58′ W)	2923	13.6–130	HF-HCl-HNO$_3$ aqua regia	[64]
Saldanha (36°34′ N, MAR)	2125–2300	6.3–40.6	HCl-aqua regia-HF-HBr	[65]
TAG (26° N, MAR)	3407–3654	2.8–113.9 *	Na$_2$O$_2$-HNO$_3$	[55]
Pacific				
South East (5°–20° S, 90°–150° W) Central North (3°–20° N, 130° W–170° E)	4000–5000	1000–2230 * 400–1000 *	HNO$_3$-HF-HClO$_4$ aqua regia	[19]
North East (5°–20° N, 119°–160° W)	4313–4529	200–577	HNO$_3$-HF-HClO$_4$ aqua regia	[20]
North East(9°30′–10°30′ N, 131°–133° W)	4000–6000	150–1150 †	NP ‡	[21]

Table 2. *Cont.*

Locality	Sediment Sample, Water Depth (m)	ΣREE, Min–Max (ppm)	Wet Digestion	Reference
North West (21°–27° N, 150°–158° E)	5720–5735	299–6800 *	HNO_3-HF-$HClO_4$ aqua regiaHNO_3-HCl-HF	[23,27]
North (21°48′–22°15′ N, 153°30′–154°07′ E)	4700–6100	5000–22,000 *	$HClO_4$-HF-HNO_3 aqua regia	[22]
Indian				
ODP sites (5° N, 90° E)	2924	0.5–1113 *	HNO_3-HF-$HClO_4$ aqua regia	[33]
DSDP and ODP sites (1°–30° S, 57°–112° E)	2832–5609	0.5–920 *	HNO_3-HF-$HClO_4$ aqua regia	[53]
Southern				
DSDP site (59° S, 104° E)	4522	72–114 *	HNO_3-HF-$HClO_4$ aqua regia	[33]

* ΣREY; † ΣREO; ‡ Not provided.

In the Mid-Atlantic Ridge, at extensive vent fields, such as Main Lilliput and Roman City (9°32′–9°33′ S, MAR) sediments are composed of Fe-Si-oxyhydroxides, goethite, and ferrihydrite [63]. Selected red sediment samples taken from both hydrothermal fields were characterized with very low contents of REE (14.4–16.6 ppm). REE distribution patterns were characterized with both negative Ce and Eu anomalies and a slight enrichment in LREE compared with HREE [63]. In the Logatchev hydrothermal field (14°45′ N, MAR), sediments contain chlorite, smectite, quartz, lizardite, and anothrite [64]. The low abundance of REE (13.6–130 ppm) exhibit a pattern of weak positive Eu and negative Ce anomalies [64]. The low ΣREE in these fields was attributed to the low-temperature hydrothermal origin of the Fe-Si-oxyhydroxides and a short contact time of precipitating fluid with ambient seawater [63,64,66,67]. Researchers claim they were precipitated from a fluid composed of seawater with hydrothermal fluid, and this was confirmed by venting fluid temperatures (<20 °C) and slightly lower concentrations of Mg in the vent fluids compared to seawater [68].

Another location explored at the MAR, the Saldanha hydrothermal field, showed similarly low levels of REE with the maximum total sum for the concentrations of the REE not exceeding the 40.6 ppm at the gravity cored sediment samples [65]. Depending on the studied depth, they were negative (Ce) or positive (Eu), which showed that the Saldanha hydrothermal field is not simply a low-temperature and diffuse venting field, as focused fluid flow occurs at this site as well [69]. In recently available results of the sediment samples gravity cored at the TAG hydrothermal field (26° N, MAR), a similar concentration of REY was found with the maximum concentration level of 113.9 ppm found in deep-sea sediments [55]. The neutrally buoyant plume overlying the TAG hydrothermal field is characterized by fine-grained Fe-oxyhydroxide particles enriched in Cd, Cu, Ni, Pb, and Zn, which are efficient REE scavengers.

In the Pacific (at 78 sites), several studies showed that sediments contained high concentrations of REE at numerous sites throughout the ES and Central North Pacific, where the total REY-rich deep-sea sediments ("REY-rich mud") were in the ranges of 1000–2230 ppm and 400–1000 ppm, respectively [19]. The results showed that sediments contained a higher HREE/LREE ratio than the current land reserves of REO, but only after more detailed sampling and analysis of the ocean-floor sediments can this hypothesis be better evaluated [19]. The estimation in the study was very promising to consider ocean-floor sediments as a relatively good resource of REY. Namely, in the selected cores collected from the Pacific, it was calculated that an area of 1 km^2 could provide up to

20% of the world annual consumption of these elements [19]. Similar values for the total REE content (200–577 ppm) and total REO (150–1150 ppm) were obtained after analysis of unconsolidated sea-floor sediment samples from the NE Pacific [20,21]. [21] estimated that the studied sediment samples comprised 37.3% of Sm, Eu, Gd, Tb, and Y, 33.5% of La and Ce, and 29.2% of Nd, Pr, and Dy, which allows them to cost twice as much as other studied samples (the polymetallic nodules and Fe-Mn crusts) [66]. Highly REY-rich sediments (2000–5000 ppm) and extremely REY-rich sediments (>5000 ppm) were found in deep-sea sediments collected from the NW Pacific Ocean within the Minamitorishima, Exclusive Economic Zone of Japan [23]. The extremely REY-rich deposits are characterized by abundant phillipsite and biogenic calcium phosphate [27].

In the North Pacific Ocean, coring deep-sea sediments contained over 5000 ppm of the total REE, and after the mineral processing method, samples with as much as 22,000 ppm of REE were recovered [22]. The authors concluded that this new resource of REE should be exploited soon, and thus can represent tremendously a much more promising resource of rare earths than on-land resources.

In addition to sediments from the Pacific, cored sediments from the Indian Ocean also contained high REY content of possible economic significance [33,53]. The next significant prospective resource of rare earths has been found in sediment samples from Deep-Sea Drilling Project (DSDP) and/or Ocean Drilling Program (ODP) sites covering a great area of the Indian Ocean [33,53]. These samples were composed mainly of siliceous ooze with zeolitic clay that contained high abundances of REY. The total concentration of REY was found to be equal to 1113 ppm, which is comparable to the levels found in the Pacific [66]. The authors found that apatite abundance was positively correlated with the sum of REY, and it was assumed that apatite played an important role as a host phase of REY in the sediments [33].

Briefly, ocean-floor sediments have not been sufficiently studied as a (future) REE (REY or REO) resource. Potentially, they can constitute a highly promising REY resource for the near future, but this must be studied in more detail. Therefore, detailed sampling and analysis are needed to properly evaluate the potential benefits at many sites within the bottom of the ocean. The promising REE-bearing sea-floor potential resource, deep-sea sediments deserve further study as possible favorable REE resources in the near future.

3.3. Economic Cost and Environmental Implications of REE Exploitation

The cut-off grade in mining operations is influenced by economic indicators of mining and recovery yield, transportation, and part of the processing of the ocean-floor sediments. Their cost-effective extraction and exploitation would leave a residue enriched in REE. Due to high price of REE, even 50% recovery after extraction will be economical. Economic benefits derived from deep-sea mining activities are to be shared for the benefit of humankind and the balanced growth of international trade [70]. Deep-ocean operations will not impact indigenous or human populations after exploitation: both must be minimal or non-existent. However, deep-sea mining must also preserve the fragile deep marine ecosystem and biodiversity.

For all earth-surface activities, disturbance or even destruction of habitat may happen, so it is important to develop environmentally acceptable practices. However, the overall environmental impact of deep-ocean seabed mineral extraction is little known, and it depends on the deposit type and extraction tools. Environmental risk assessments should be always considered a priori exploitation, and this practice should be an essential part of the decision-making process [16,71–73]. The value of an environmental risk assessment is ultimately associated with the evaluation of environmental managers about a project [71]. The deep-sea mining should demonstrate its commitment to prevent serious environmental harm by complying with legal requirements, using good practice and thus minimizing environmental impacts [72,73]. Recently, six components of good practice that could improve deep-sea mining were proposed, and the International Seabed Authority will need to develop additional rules, regulations, and procedures to assure decision concerning the

common heritage resources of the areas beyond national jurisdiction (the Area) [74]. The new alternative areas should be prioritized by enhanced scientific research [75].

The damage will occur in the habitat in the path of a mining vehicle, and sediment plume of unknown extent will be created in the bottom-water layer [56]. Nevertheless, it is hard to predict the impact on the surrounding biodiversity and the risk of species because of limited knowledge of the distribution of species [3]. Additional environmental studies are needed before large-scale, commercial exploitation starts; this may include a moratorium on deep-sea mining. Detailed discussions for the funding, planning, and implementation of the strategic goals by International Seabed Authority and the scientific community are crucial to address in the near future, both for rising the deep-sea mining in the Area and to protect the environment.

4. Conclusions

Given that the demands for the REE are growing rapidly, and their economic trade is limited, abundant resource potentials of the rare earths in the global ocean-floor unconsolidated sediments may be an alternative solution for their supply. Reported high concentrations of REE in sea-floor sediments (in Indian and Pacific Oceans ranging up to ≈ 1100 and 22,000 ppm, respectively) guarantee future detailed exploration and studies of their resource potential. To ensure a truly global supply of REE and other critical metals, to enable the advancement of a wide range of REE applications necessary for the transition to a low-carbon future, new sources of these strategic, highly valuable metals will be imperative, and many innovative ideas for their extraction should be considered. For the time being, more than immediate large-scale ocean-floor mining, we need readiness followed by implementing assessment.

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