Rare Tales from the Deep Seas

The history of deep-sea mining is rich with tales of international subterfuge, espionage and growing alarm at the imbalance of global access to critical metals and rare-earth elements—increasingly precious commodities. I briefly discuss the seabed distribution, elemental composition, and common uses of rare-earth elements. Other strategic seafloor mineral deposits such as cobalt crusts and seafloor massive sulfide (SMS) deposits, or shallow methane gas hydrates, will be considered in a future article.

Metals, Metals Everywhere

Any future transition to large-scale dependence upon electric vehicles and wind turbines will require significant volumes of special metals like cobalt (Co), lithium (Li), tellurium (Te) and neodymium (Nd), as well as base metals like iron (Fe), copper (Cu), lead (Pb) and zinc (Zn), and rare-earth elements. Global attention in recent years has turned to various elemental deposits that lie loosely on the seabed or buried shallowly in the sediment, and that can in principle, be recovered fairly easily using methods to harvest polymetallic nodules or materials dissolved in hot fluids ejected by seafloor hydrothermal vents.

Manganese nodules are polymetallic concretions that are long known to contain high concentrations of cobalt, nickel (Ni), copper, manganese (Mn) and other metals—yield 99% usable mineral content--and are abundant on the abyssal plains of the deep ocean between 4,000- and 6,000-meters depth.

Rare-earth elements—the focus of this newsletter—also occur in particular abundance in such nodules. It was estimated in a prominent Nature journal article a decade ago that an area of 1 square kilometer around a hotspot near Hawaii could hold 25 000 tons of rare-earths. Other estimates suggest that the Clarion-Clipperton Zone, about the size of Europe, and extending from the west coast of Mexico to Hawaii, holds more than 27 billion tons of nodules containing of the order of 7 billion tons of manganese, 340 million tons of nickel, 290 million tons of copper and 78 million tons of cobalt, as well as rare-earths. Other important areas include the Peru Basin, the Penrhyn Basin near the Cook Islands, and the central Indian Ocean. Overall, the ocean floor might hold more than the 110 million tons of rare-earths estimated to be buried on land.

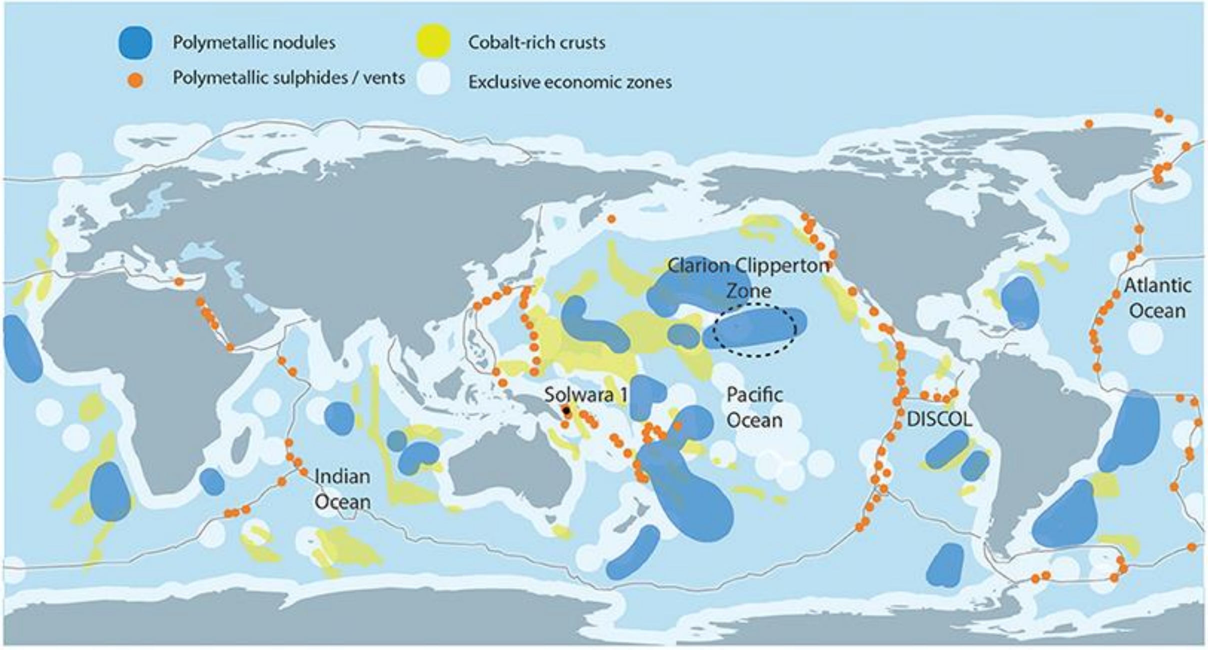

Figure 1. Global distribution of known seabed minerals. From Miller et al. (2018).

Howard Hughes, the Cold War, Nuclear Missiles, and Deep Sea Mining

Using the cover story of mining for seafloor manganese nodules, and backed by the CIA, Howard Hughes built the Hughes Glomar Explorer, which attempted to recover the Soviet submarine K-129 (and its payload of R-21 nuclear missiles) from the Pacific Ocean floor in 1974. Project Azorian was one of the most complex, expensive, and secretive intelligence operations of the Cold War at a cost of about $800 million, or $4 billion today. Only part of K-129 was ultimately recovered, and time will tell whether this expensive mission was an omen for commercial deep sea mining half a century later.

As noted below, the global production of rare-earth oxides is limited to a handful of dominant players, with China having by far the greatest share. Attention has naturally turned to the untapped resources below the oceans. Seabed mineral activities in international waters are regulated by the Jamaica-based United Nations' International Seabed Authority (ISA), however, Norway is pressing ahead with plans to develop large-scale seabed mining activities within the next decade after several years of investigations by the Norwegian Petroleum Directorate.

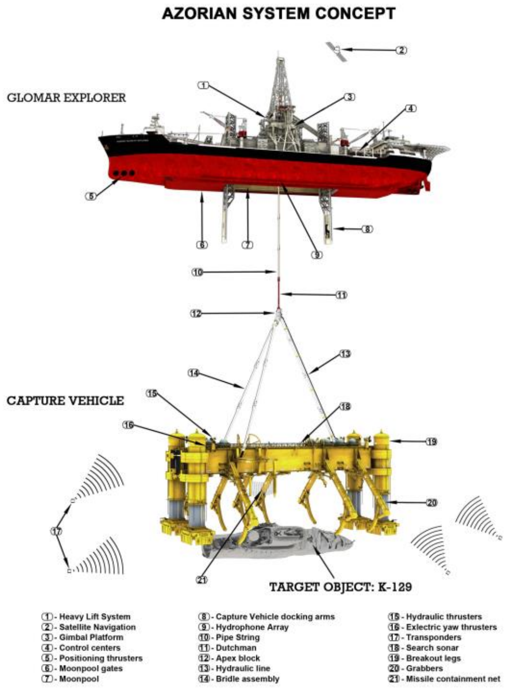

Figure 2. Computer-generated image depicting the capture vehicle being lowered from the open moon pool of the Hughes Glomar Explorer. From the U.S. Naval Institute.

Polymetallic deposits of copper, zinc, cobalt, gold, silver, lithium and the rare-earth metal scandium have been mapped in Norwegian waters along the Mid-Atlantic Ridge between Jan Mayen Island and the Svalbard archipelago in the Norwegian Sea as far as 700km offshore. The environmental impacts of seabed mining are not yet understood, but the rapid expansion of Norwegian firms scaling up for full-scale operations will provide the first insights into the interaction between mining and the seabed environment.

If such mining efforts are proven to be commercially viable, might a new seafloor cold war break out amongst the global players jostling for access to resources in international waters? Special metals and rare-earth elements are critical to all economies and increasingly used in producing defense assets.

Rare-Earth Elements: Outcasts from the Periodic Table

The rare-earth elements, also called the rare-earth metals or rare-earth oxides, or the lanthanides (though yttrium and scandium are usually included as rare-earths), are a set of 17 nearly indistinguishable lustrous silvery-white soft heavy metals (refer to Figure 3). Scandium and yttrium are considered rare-earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties but have different electronic and magnetic properties. All are naturally occurring except promethium, which is radioactive, and the most stable isotope only has a half-life of 17.7 years. What makes the rare-earth elements trickier to harness than other elements are the fact that they are dispersed fairly broadly, which means that the process of acquiring them is often labor and energy-intensive—hence the 'rare' label.

Despite their name, rare-earth elements are relatively plentiful in Earth's crust, with cerium being the 25th most abundant element at 68 parts per million—more abundant than copper—and the 16 naturally occurring rare-earths fall into the 50th percentile of elemental abundances. During the 160 years of discovery (1787–1947), the separation and purification of the rare-earth elements was a difficult and time-consuming process. Because the rare-earth elements were found to be fission products of the splitting of a uranium atom, the U.S. Atomic Energy Commission made a great effort to develop new methods for separating the rare-earth elements. However, in 1947 Gerald E. Boyd and colleagues at Oak Ridge National Laboratory and Frank Harold Spedding and colleagues at the Ames Laboratory in Iowa simultaneously published results which showed that ion-exchange processes offered a much better way for separating the rare-earths.

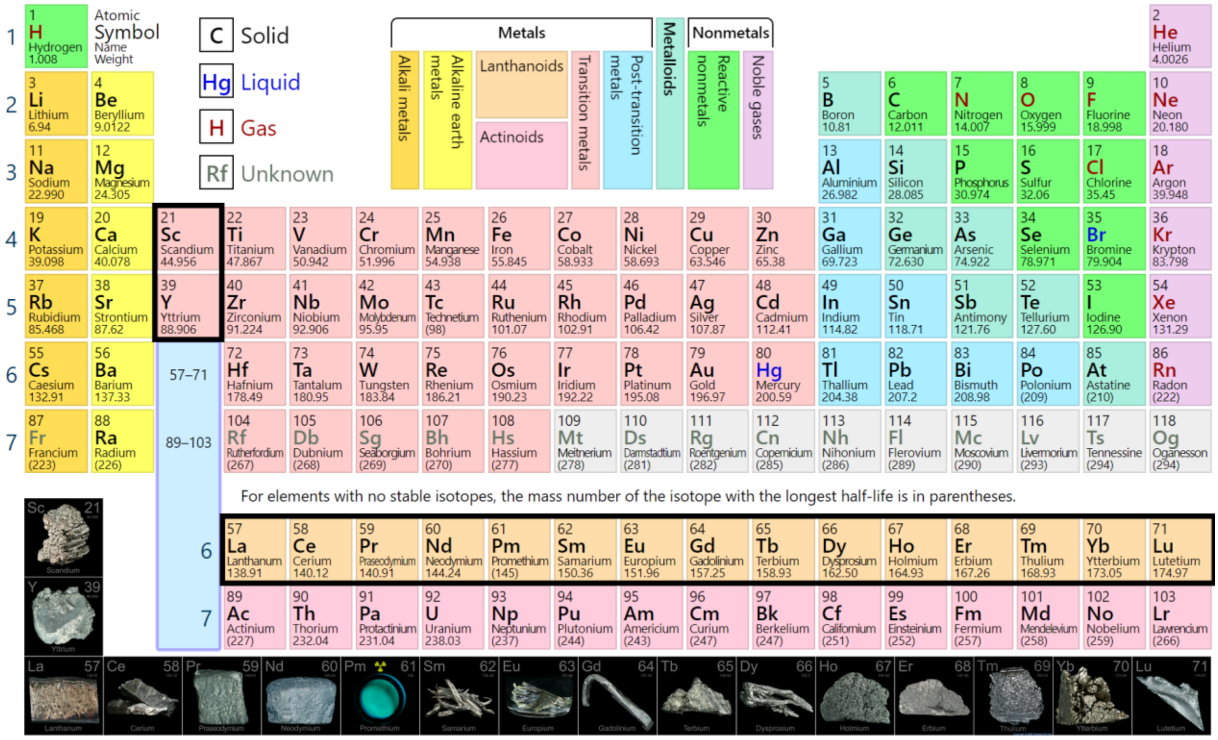

Figure 3. Periodic table of the elements, with the rare-earth elements Sc, Y, La, and the lanthanides from Ce to Lu, highlighted by thick black borders, and photos of refined rare-earths are shown along the bottom. The row of 15 consecutive elements below the lanthanides is the actinides (from actinium to lawrencium: atomic numbers 89–103), and all are radioactive.

Of the approximately 160 minerals that are known to contain rare-earths, only four are currently mined for their rare-earths: bastnasite, laterite clays, monazite, and loparite. The commercial viability of seabed mining is not yet proven, but several companies are actively preparing to pursue full-scale activity.

Many people do not realize the enormous impact the rare-earth elements have on their daily lives, but it is almost impossible to avoid a piece of modern technology that does not contain any. Even a product as simple as a lighter flint contains rare-earth elements. Their pervasiveness is exemplified by the modern automobile, one of the biggest consumers of rare-earth products. Dozens of electric motors in a typical automobile, as well as the speakers of its sound system, use neodymium-iron-boron permanent magnets. Electrical sensors employ yttrium-stabilized zirconia to measure and control the oxygen content of the fuel. The three-way catalytic converter relies on cerium oxides to reduce nitrogen oxides to nitrogen gas and oxidize carbon monoxide to carbon dioxide and unburned hydrocarbons to carbon dioxide and water in the exhaust products. Phosphors in optical displays contain yttrium, europium, and terbium oxides. The windshield, mirrors, and lenses are polished using cerium oxides. Even the gasoline or diesel fuel that propels the vehicle was refined using rare-earth cracking catalysts containing lanthanum, cerium, or mixed-rare-earth oxides. Hybrid automobiles are powered by a nickel–lanthanum metal hydride rechargeable battery and an electrical traction motor, with permanent magnets containing rare-earth elements. In addition, modern media and communication devices—cell phones, televisions, and computers—all employ rare-earths as magnets for speakers and hard drives and phosphors for optical displays. The amounts of rare-earths used are quite small (0.1–5 percent by weight, except for permanent magnets, which contain about 25 percent neodymium), but they are critical, and any of those devices would not work as well, or would be significantly heavier, if it were not for the rare-earths.

Some Curious Properties

For most parts of the periodic table, when you move from one element to the next you add a new valence electron each time, giving each new element unique properties. But in the rare-earths, electrons are being added to a deep inner shell instead: every one of the rare-earths from 57 to 71 has a filled ‘6s’ outer electron shell, and differing numbers of the deep ‘4f’ shell, which contributes only minimally to chemical properties.

Because the outer electron shell has the same configuration for each of the rare-earths, their chemical properties are all similar. But magnetic properties follow an entirely different set of rules that involve all the electrons, not just the outer shell.

Terbium (Tb) and dysprosium (Dy) form a magnetostrictive alloy with iron known as Terfenol-D: it expands and contracts in a magnetic field, and has found particular application to low frequency, high powered underwater acoustics such as naval sonar systems. PGS developed a new marine vibrator source for shallow water acquisition for PGS Onshore in 2007 with a new driver concept using Terfenol-D. It showed good reliability but did not create the flat frequency response that we expected. This technology was licensed to a third party in 2010 for non-streamer work in shallow water.

Less exotic applications of rare-earth elements for their unique magnetic properties involve holmium (Ho), gadolinium (Gd), neodymium (Nd), and samarium (Sm). Holmium has the highest magnetic moment of all elements and is used as a magnetic flux concentrator for magnetic resonance imaging (MRI). Coincidentally, gadolinium enhances the quality of MRI by altering the magnetic properties of adjacent water molecules in the body and is used as a contrast agent for MRI scans. Neodymium makes the most powerful permanent magnetics when used in alloys with iron and boron, and samarium-cobalt magnetics operate at higher temperatures than neodymium magnets, making them ideal for electric-guitar pickups.

Another notable application of rare-earth elements is to laser technology, where the fiber inside is doped with rare-earth elements. Erbium is amongst the most commonly deployed, although other elements used include neodymium, holmium, thulium, ytterbium and praseodymium. The type of element chosen may also impact the nature of the host glass used; for example, erbium can be found in silicate, phosphate and fluoride glasses, while something like ytterbium is usually limited solely to silicate glass as the host.

Rare-earth elements are particularly advantageous because of the way that they absorb and fluoresce across specific portions of the spectrum, allowing them to amplify the laser pump source effectively. Little of the useful light is lost, so fiber laser systems can be highly efficient, requiring less power than alternative gas or crystal laser solutions. Another advantage of using rare-earth elements in fiber lasers is that they can survive for long periods of use without the need for any kind of maintenance or outside intervention. This further reduces operating costs and means that even with high energy output, rare-earth element doped fiber lasers are resilient and reliable in the long term. Collectively, fiber lasers doped with rare-earth elements are well suited to deployment in industrial environments where their power, precision and resilience are all desirable.

At a somewhat more mundane level, thulium, the least abundant rare-earth element (but more abundant in the earth than cadmium, silver or gold), is used in arc lighting to produce the green emission line that is not emitted by other elements.

Note that although I focused here upon the more novel applications of rare-earth elements, according to the USGS, the global estimated distribution of rare earths by end use was as follows: catalysts (75%); ceramics and glass (6%); polishing (5%); metallurgical applications and alloys (4%); and other (10%).

Global Production of Rare-Earths

According to the USGS, China dominates global reserves (44 million MT) and production of rare-earths (140 00 MT), with the US a distant #2 in at 1.4 million MT in reserves and 38 000 MT in production, respectively. The next largest producers are Myanmar, Australia, Madagascar, India and Russia. Given the global geopolitical climate, it is understandable why the major economic powers increasingly seek to engage in seabed mining for minerals critical to their economy and used in producing defense assets.

Potential Roles for Marine Geophysics

I primarily focused upon the uses of rare-earth elements in this short article—most commonly hosted within polymetallic seafloor nodules. However, cobalt crusts that form on the flanks of seamounts, and seafloor massive sulfide deposits or SMS deposits that form in the deep ocean around submarine volcanic arcs where hydrothermal vents exhale sulfide-rich mineralizing fluids into the ocean, are also significant candidates for seafloor mining operations. Methane gas hydrates hosted at shallow depths may also be commercial mined in the future.

In all such scenarios, the complementary use of surface-based geophysical methods such as high-resolution seismic; and autonomous underwater vehicle (AUV) measurements of shallow acoustic, electromagnetic and chemical properties; will expectably play important roles in characterizing the near surface. A variety of environmental monitoring pursuits are also expected to be necessary to quantify the impact of seafloor mining on various marine fauna ecosystems.