REVIEW

Rare earth elements: Mendeleev's bane, modern marvels

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The rare earths (REs) are a family of 17 elements that exhibit pronounced chemical similarities as a group, while individually expressing distinctive and varied electronic properties. These atomistic electronic properties are extraordinarily useful and motivate the application of REs in many technologies and devices. From their discovery to the present day, a major challenge faced by chemists has been the separation of RE elements, which has evolved from tedious crystallization to highly engineered solvent extraction schemes. The increasing incorporation and dependence of REs in technology have raised concerns about their sustainability and motivated recent studies for improved separations to achieve a circular RE economy.

The archaeological three-age system (Stone, Bronze, and Iron) organizes the history of humankind according to the central role of metals in technological evolution. From antiquity to the modern day, the exploitation of metals has required technologies for their mass extraction and purification, creating strategic importance for mineral deposits and metallurgical knowledge. Unlike other resources, metals are relatively amenable to recycling and to the creation of circular supply chains (*1*). This scenario is evident in historical developments for Fe, Cu, Al, Ti, Zn, Ni, and Sn with recycling rates representing between 15 and 70% of the current usage for those metals in the United States and the European Union (*2*, *3*). However, in recent decades, new technologies have emerged that rely on metals of previously limited use: lithium, cobalt, and the rare earth (RE) elements, among others. Rare earths are finding increasing use in communications—and display devices, renewable energy, medicine, and other practical applications that affect daily life. In this Review, we examine the past and present separation methods that have developed REs into an industrial sector, with a focus on recent advances.

Conceptually, a chemical separations process implies the selective transfer of one compound between phases. This enrichment is achieved by the evolution of a chemical or physical property in a monotonic (solubility, affinity) or variable (redox, speciation) fashion. An efficiency of the separation is typically characterized by a separation factor, that is, the product of the molar enrichment factors of each phase. Rare earth separation relies mostly on subtle, monotonic changes in thermodynamic properties, rendering their separations particularly difficult (Fig. 1 and Box 1).

Discoveries of the REs: Crystallization and precipitation techniques

In 1869, only six REs had been "discovered" (*4*), and their existence was challenging Mendeleev's revolutionary theory of elemental periodicity. In his seminal *Attempted System*, REs were already grouped separately, in an apparent disconnection with the rest of the periodic table (*5*, *6*). To accommodate some of these troublesome elements, Mendeleev himself examined and confirmed their trivalent natures in oxides (RE_2O_3), materials that were initially assumed to be divalent. In the latter iteration of his *Natural System of the Elements*, Mendeleev tried to accommodate the known REs in analogy to the d-block metals, but this placement led to inconsistencies. Ultimately, Mendeleev never successfully set the REs in his periodic system, a frustration that may have contributed to his shift in research interest away from the periodic table after 1871 (*6*). Without easily discernable periodic trends, and owing to the limited characterization techniques of the time, close to 100 erroneous new RE claims were made during the last part of the 19th century (*7*). By 1907, all REs had finally been isolated, with the exception of nonnaturally occurring Pm that was human-made in 1947. After 1913, the development of Bohr's atomic model and Moseley's x-ray spectroscopy studies finally rationalized the position of the f-block in the periodic table. Never in the history of chemistry had a large family of elements been so defined by the separation of its individual components. This historical challenge remains a defining characteristic of the REs. From a thermodynamic standpoint, the chemical similarity of REs leads to only minor differences in the binding affinity of a given ligand. For example, a difference of <1.5 kcal mol^{-1} is observed for adjacent REs in binding with a classical chelate such as $EDTA^{4-}$ (Fig. 1A). The associated modest change in ionic radii across the RE^{3+} cations does not promote strong partitioning based on speciation, underlying the difficulty of RE separation by crystallization and precipitation methods. Nevertheless, tedious sequences of recrystallization were the only methods available for the separation of REs until the first half of the 20th century (*8*). Such methods provided limited quantities of material of often mediocre purity, limiting the study and application of REs (*8*). Auer von Welsbach, who discovered Pr and Nd and codiscovered Lu, was the first to develop an industrial process in 1887 to produce lanthanum, cerium, and thorium oxides by fractional crystallization, for their use in the fabrication of incandescent gas mantles (*9*). These early methods have now been surpassed industrially (see below), but chemists' toolboxes have evolved, and new separation methods based on controlled coordination chemistry have been demonstrated recently, in particular for targeted separation applications. The ability to site-differentiate two REs in a molecule is a challenge that was tackled with supramolecular systems by Bünzli and Piguet. Using dipotic receptors ligands, they pioneered the self-assembly formation of heterobimetallic helicates of general formula $[(HRE)(LRE)(L)_3]^{6+}$, through an allosteric response as the selectivity mechanism (*10*). Other groups employed self-assembly principles to form homo- or heterobimetallic helicates with good RE selectivity (*11*, *12*). Bünzli and Sun described the rapid self-assembly of homotetrametallic tetrahedral coordination cages; the supramolecular cooperativity in this system led to very efficient "self-sorting" of RE pairs, even adjacent ones. Ligand functionalization with hydrophobic chains allowed separation by a solvent extraction procedure, a unique example based on supramolecular cooperativity (*13*). The self-sorting of REs to maintain the regularity of a growing crystalline phase can also be exploited in coordination polymers and metal-organic frameworks (MOFs) (*14*, *15*). Yin, Wang, and co-workers reported the formation of multiple RE-borate coordination polymers (*16*). Six successive crystalline phases were observed depending on the identity of the RE, an unusually large number across the series of REs. By exploiting the different flotation properties of the crystalline phases, the authors separated Nd from Dy with a separation factor approaching 1000. However, the separation of adjacent lanthanides was limited.

Our group achieved selectivity in RE separations by leveraging a chelating tripodal ligand bearing a size-sensitive molecular aperture. Discrimination of LREs and HREs was based on that property, permitting the separation of Nd/Dy and Eu/Y by filtration with separation factors of 300 and 190, respectively (*17*–*19*). Tasaki-Handa also reported a separation method for acidic aqueous solutions of Nd/Dy; addition of dibutylphosphate led to the crystallization of a coordination polymer enriched in dysprosium with a separation factor above 300 (*20*). In addition, the authors have presented a simple thermodynamic model for the separation, providing a method for optimizing the separation conditions a priori.

Chromatographic separations

World War II and the associated development of military and civil nuclear sectors marked the birth of industrial RE separation (*21*). The first breakthrough in the large-scale production of purified REs was the introduction of chromatographic techniques in the 1950s. These methods were the primary source of pure REs

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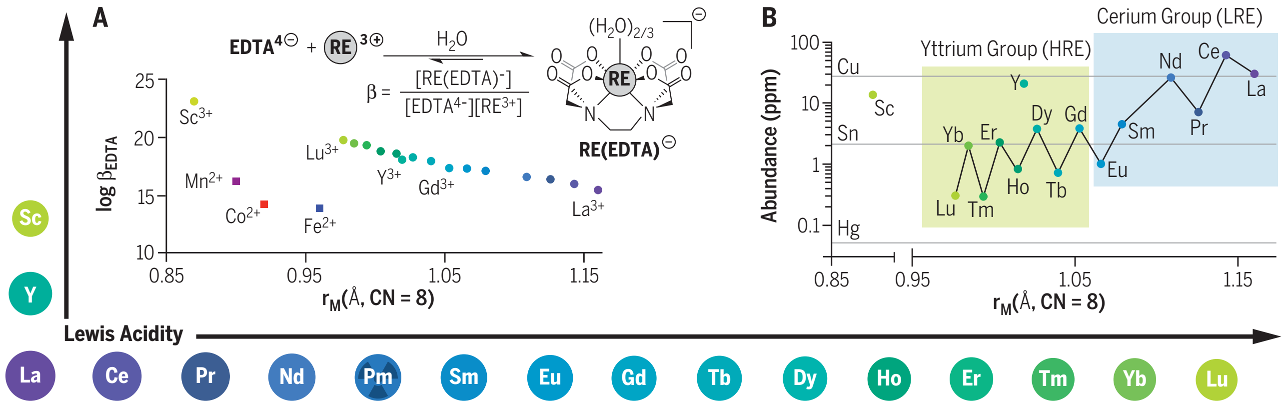

Fig. 1. Periodic classification of the REs with spheres scaled to the ionic radius of RE^{3+}. Insets: (**A**) Stability constant of RE(EDTA)$^-$ complexes compared with their ionic radii; values for some divalent transition metals are plotted for comparison (*83*). (**B**) Plot of upper crustal abundance of REs against their ionic radii and approximate boundaries of the mineralogical groups (*71*).

Box 1. Properties of the rare earth elements.

The REs are a family of 17 metallic elements formed by the group III (Sc, Y) and the lanthanide series (La–Lu). The name "rare earth" is misleading and does not represent a geological scarcity (Fig. 1B) (*71*). The origin of this description lies in the occurrence of REs as a mixture of elements in minerals, generally at low concentration. In ore deposits, REs are generally separated into two groups designated as the cerium group [or light RE (LRE)] and the yttrium group [or heavy RE (HRE)]. Though dispersed worldwide, only few deposits exist with economically viable concentrations (*72*). Chemically, REs demonstrate very similar properties with the prevalence of the +3 oxidation state under ambient conditions, a large electropositivity, and kinetic lability. They are strong Lewis acids and present a continuous and steady decrease in the size of their atomic and ionic radii along the lanthanide series (the so-called lanthanide contraction) caused by the gradual population of the f-electron shell. The contracted, core-like nature of the 4f valence orbitals engenders an almost purely ionic chemical bonding situation. Consequently, they do not present any substantial crystal field effect, causing large coordination numbers (CN, typically 8 to 12) and nondirectional metal-ligand interactions governed by steric effects. The conjunction of these attributes explains the difficulty of separating REs.

before the advent of solvent extraction and employed the differential affinities of a solution of RE (the mobile phase) with a stationary phase. Groundwork conducted by Spedding for the Manhattan project demonstrated the scalable resolution of REs on cation-exchange sulfonated resins. The bare resin had a similar affinity for all REs. The loaded column was eluted with a competitive chelating eluent (ammonium citrate), and the more Lewis acidic HREs were preferentially eluted, leading to separation in reverse order to atomic number (*22*). Later iterations of the method used EDTA and derivates as the chelating eluents, allowing separation of all REs with good purities. Other approaches focused on extractive chromatography, where an extractant was impregnated or covalently linked to the stationary phase (*23*).

Recent work in chromatographic separation has promoted the discovery of new stationary phases. Binnemans and Roosen have investigated EDTA-functionalized biopolymers for chromatographic separations at low pH (*24*). Kleitz and co-workers have reported new carbon- and silica-based mesoporous materials that show selective RE sorption (*25*). By grafting neutral extractant across the pores, they obtained notable "bell-shaped" RE distribution curves and confirmed a selectivity mechanism principally tied to the RE sizes (*26*, *27*). A related approach is the synthesis of RE-imprinted mesoporous silica, demonstrating preferential sorption of the templating RE (*28*). Similarly, Zhang *et al.* synthesized a new functionalized titania material by controlled hydrolysis (*29*). The separation factors were excellent for Nd/Dy (>2000) and adjacent pairs (>15). The study proposed an unusual separation mechanism whereby the surface TiO^{2+} groups were transmetallated by the RE^{3+} cations. Because of the small size of the Ti^{4+} cation (0.61 Å, CN 6), the smaller HREs were more likely to fill the lacunar host matrix. The ability of MOFs to preferentially adsorb REs has also been examined (*30*). The separation factors were limited, but notably, the selectivity for HREs was reversed to that for LREs when the organic linker was modified. Grafting of extractants on core-shell magnetic nanoparticules was also proposed, allowing for good separation, large uptake, and fast decantation (*31*, *32*).

Mass production: Solvent extraction

Separation by solvent extraction relies on a simple chemical principle: A ligand or extractant (Fig. 2A) is dissolved in a water-immiscible organic solvent, typically kerosene, and contacted with an aqueous, acidic concentrate of REs (Fig. 2B). Upon mixing (Fig. 2C), the REs are transferred to the organic phase by coordination with the extractant at the liquid-liquid interface (Fig. 2D). After settling the mixture, the transfer can lead to selective partitioning of the REs between the two phases, according to their respective affinities for the extractant following Lewis acidity trends (Fig. 1A). For neighboring REs, the separation factor over one step is typically small. But the operation is repeated in an interlinked, countercurrent mode (Fig. 2E), concentrating the HRE in the organic phase and LRE in the aqueous raffinate. Multiple parameters are tuned to optimize separation, but the most critical is a selective extractant that reduces the number of iterations required. The development of actinide separation processes directed attention toward phosphorus-based extractants. By analogy with the PUREX process, tributylphosphate (TBP, Fig. 2A) was recognized as a powerful extractant for Ce^{IV} and trivalent REs (*33*). In 1957, Peppard and co-workers reported that trace contamination of TBP by its hydrolyzed phosphoric acids caused discrepancies in the RE separation results, leading to the discovery of HDEHP (Fig. 2A) (*34*). This extractant was proposed to coordinate by a proton exchange, likely forming a 1:6 complex with the formula $[RE(H(DEHP)_2)_3]$ (Fig. 2D). Within 10 years, Molycorp and Rhône-Poulenc developed industrial processes and plants to separate RE-rich ores such as bastnäsite, monazite, and xenotime (Fig. 2B). Especially through the efforts of Xu Guangxian and producers in the People's Republic of China (PRC), the Western companies were joined by Chinese producers that are now responsible for ~90% of the worldwide production. Efforts in the PRC also produced the major recent improvements in separation process optimizations (*35*).

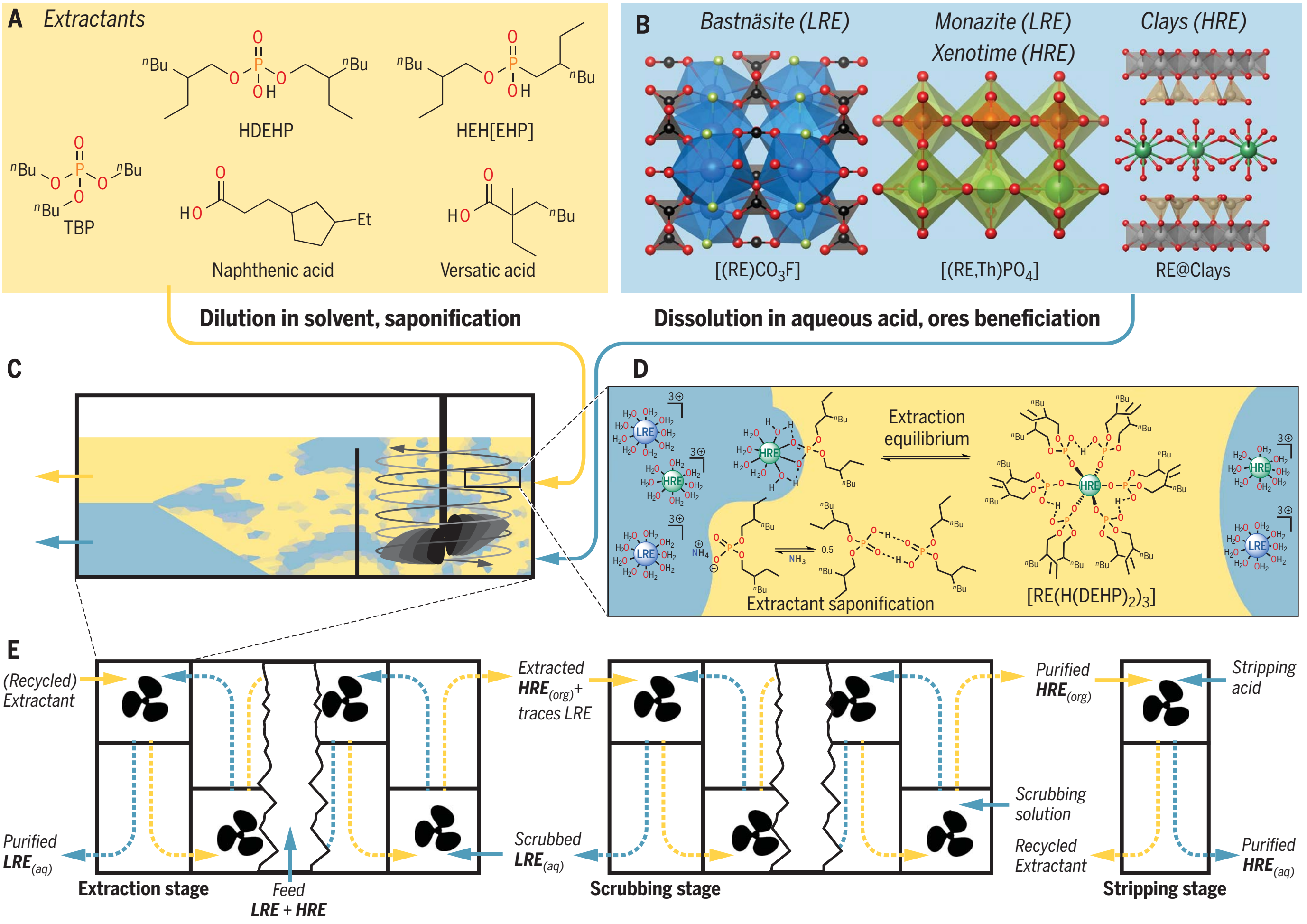

Fig. 2. Solvent extraction. (**A**) Commonly used extractants. (**B**) Typical RE-containing minerals. (**C**) Cut-off side view of a simple mixer-settler unit. (**D**) Schematic extraction equilibria. (**E**) Flow chart (top view) of batteries of mixer-settlers in a model industrial process with extraction, scrubbing, and stripping stages.

Exact details of the industrial processes vary depending on the ore composition, but a general solvent extraction scheme can be subdivided into extraction, scrubbing, and stripping (Fig. 2E). At the extraction step, a high organic uptake of the targeted RE is desired, and selectivities of adjacent metals are consequently limited. In the scrubbing steps, the extracted REs are washed with a fresh or acidic aqueous feed to selectively back-extract impurities. Finally, the stripping step back-transfers the purified RE in the aqueous phase and recycles the extractant and the organic solvent. In practice, these steps are repeated multiple times to achieve the targeted purity. A typical separations plant has hundreds of mixer-settler units that are arranged in a hyperlinked network aimed at reducing energy and chemical consumption, the two main drawbacks of solvent extraction (*36*). Although researchers have focused on designing more selective extractants, volume and cost considerations have kept neutral organophosphates, acidic organo-phosphoric and phosphonic acids, and some carboxylic acids as the most commonly used extractants (Fig. 2A). Synergistic effects from mixtures of these simple extractants can create specialized mixtures that perform better for HREs or LREs (*35*, *37*). Most extractants are cation-exchangers, creating a large dependence of the extraction equilibrium on pH, typically adjusted with aqueous ammonia. The discharge of these various aqueous effluents has substantial soil and groundwater contamination and eutrophication consequences. Process optimizations help limit the use of aqueous ammonia, reducing consumption from seven to about one or less ton per ton of RE oxides (*35*). Mathematical modeling of solvent extraction has emerged as a critical tool to optimize any viable process. Following work by Alders, Xu and Yan developed a milestone theory of countercurrent extraction that allows optimization of most process parameters (*35*, *37*). Advanced dynamic simulations are now supported with in-line analysis that further improves predictions. To refine these models, it is critical to understand the basic transfer mechanism and metal speciation during the extraction. Studies by Jensen, Ellis, Antonio, Lumetta, and others demonstrated that the classical 1:6 RE:extractant complex (Fig. 2D) was not always formed in solution (*38*–*41*). Bu, Soderholm, Schlossman, and Qiao examined the transport of ions at the interface by experimental and simulations approaches (*42*, *43*). Kinetic studies and modeling of the mass transfer at these interfacial regions are similarly attracting attention (*44*). Microsolvation and weak interactions are also critical to determine the separation efficiency (*45*–*47*). Works by Dourdain, Dufrêche, Pellet-Rostaing, and Zemb shed light on the formation and behavior of weak aggregates and their importance in the optimization of solvent extraction processes (*48*–*50*). A clear, practical motivation exists for these studies because the formation of a third phase, reversed micelles, or stable emulsions can reduce the extraction efficiency and often requires the addition of modifiers that increase chemical consumption. Ionic liquids provide another opportunity to tackle problems linked to the volatility and flammability of organic solvents (*51*).

Redox methods

Rare earths are characterized by the prevalence of the trivalent oxidation state; however, some electronic configurations stabilize the divalent

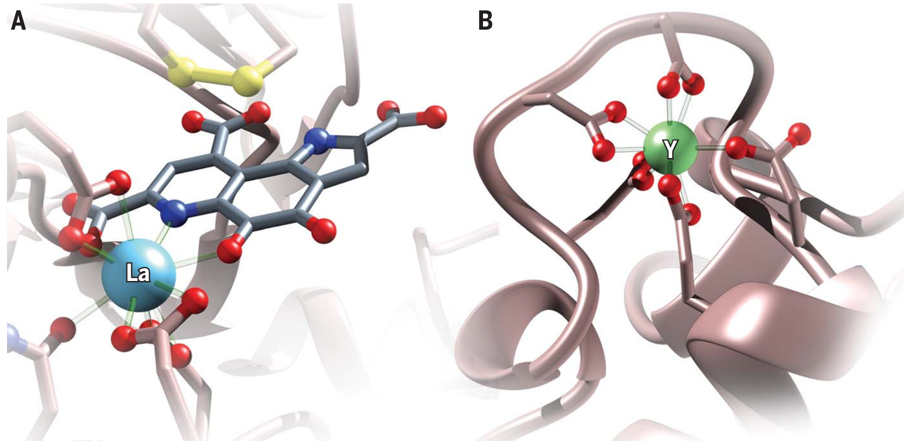

Fig. 3. REs in biology. (**A**) La-MDH active site (PDB 6DAM); (**B**) Y-lanmodulin binding site (PDB 6MI5) (*62*, *66*).

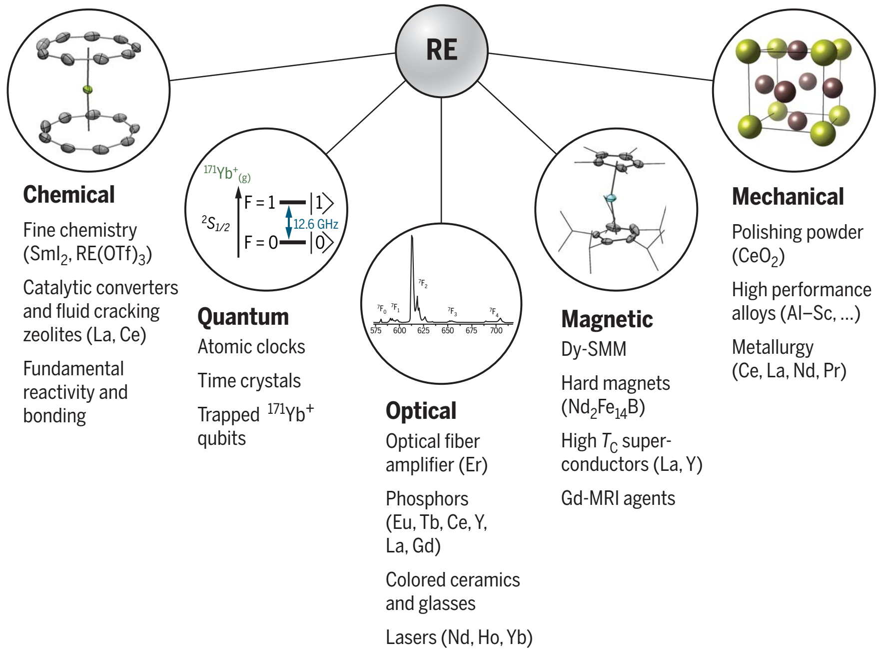

Fig. 4. Selected applications and research areas for REs. Illustrations: a linear thulium sandwich complex (*73*); partial energy diagram of a $^{171}Yb^+$ ion (*80*); luminescence spectrum of a Eu^{3+} cation (*85*); a Dy-SMM (*77*); an Al_3Sc unit cell found in high-performance alloys (*84*).

Box 2. Similar but unique.

Although REs have notable chemical similarities, the gradual filling of the f-orbitals makes them unique for many applications. As summarized in Fig. 4, the mechanical, chemical, optical, and magnetic properties of REs are exploited in various industrial and technological sectors, and in certain research areas. The shielded nature of the f-orbitals leads to well-defined energy levels that are weakly perturbed by the environment and are accompanied by large spin-orbit coupling, which enable application of REs in optical and magnetic applications. Numerous challenges still exist in the fundamental understanding of the f-orbital interactions with ligands (*73*–*75*). Recent progress in the synthesis of high-temperature single-molecule magnets (SMM) or unconventional superconductors are further highlighting the vitality of research on REs for tomorrow's technologies (*76*–*78*). REs also have attracted considerable attention for the design of quantum devices (*79*). In particular, the nuclear spin-bearing (I = ½) $^{171}Yb^+$ gas-phase ion has been applied in high-precision atomic clocks, and more recently, in pearl chain-trapped qubits (*80*). Related work has also revealed exotic phenomena such as time crystals or quantum teleportation (*81*, *82*). Notably, ultrapure materials are required for these studies.

(Eu^{II}, $4f^7$) or the tetravalent (Ce^{IV}, $4f^0$) states under ambient conditions. These properties are employed to facilitate the separation of these elements. In most industrial processes, ores are typically oxidatively roasted, forming Ce^{IV} salts that are removed as an insoluble residue [$Ce(OH)_4$ or CeO_2]. Europium occurs in small quantities in the mined minerals and cannot be efficiently reduced early in the separation process. In the reported Molycorp process, after concentration by solvent extraction, an aqueous feed enriched in Eu^{3+} was reduced over a zinc amalgam column and subsequently precipitated as $Eu^{II}(SO_4)$, leaving the other REs in solution (*8*, *52*). Europium and cerium also have notable photoredox properties that are being investigated for catalysis (*53*–*55*). Donohue identified these characteristics as a potential mode for separations (*56*). In 2015, Van Gerven and colleagues reported excellent photoseparation of Eu/Y derived from red phosphors containing only doped quantities of Eu (*57*). All REs can actually be reduced in solution to their divalent state (*58*). However, the extreme reactivity of these reduced compounds is not yet practical for separation. In the solid state, the reductive chemistry of REs can, however, be exploited for the purpose of separation. As reported by Uda, $NdCl_3/SmCl_3$ were separated by selective Al reduction of $SmCl_3$ to $SmCl_2$ at 800°C. Subsequent vacuum distillation at 1000°C afforded the more volatile $NdCl_3$ with a separation factor estimated at 570, an impressive value for nearly adjacent REs (*59*). The above methods have focused on the RE redox chemistry; however, our group has demonstrated that the increasing Lewis acidity of the REs can affect the irreversible oxidative electron transfer rate of a coordinated redox-active ligand (*60*). In this case, the selectively oxidized complexes were separated by filtration. The kinetics underpinning the separation allows for construction of a model to predict the separation factors based on the cyclic voltammograms of the isolated complexes. Notably, this work demonstrated a rare application of kinetic principles for RE separations.

Biology: A new avenue for separation

Rare earths are used extensively in medicine, especially as imaging agents. But until recently, they were believed to have no natural, biological importance. Surprisingly, Jetten, Op den Camp, Pol, and co-workers reported in 2014 an essential dependence of methanotrophic bacterium on LREs. They rationalized this requirement by the replacement of the generally encountered Ca^{2+} cation by a LRE^{3+} cation in the active site of the methanol dehydrogenase (MDH) enzyme (*61*, *62*) (Fig. 3A). Following that discovery, RE-dependent bacteria have been found in many environments and have initiated a new field of research (*63*, *64*). Owing to the low concentration of soluble REs encountered in nature, especially compared to Ca, there are interesting questions on the mechanisms of their selective uptake and transport. Recent work by Cotruvo *et al.* has shed new light on this aspect by purifying, from RE-dependent bacteria, a protein able to bind REs with a 10^8-fold selectivity over Ca (*65*). The protein, named lanmodulin, appears to be derived from the well-established calcium analog calmodulin, but with substantial structural differences (*66*) (Fig. 3B). Both the RE-MDH and lanmodulin have demonstrated RE selectivity for the more abundant LREs. For MDH, catalytic activity is evidently based on a balance between Lewis acidity to activate the associated PQQ cofactor and cation size to facilitate the substrate coordination, factors that culminate with Pr (*67*). Preferential binding of LREs was also noted for lanmodulin, a feature that is rarely observed in RE coordination chemistry. This RE-bioinorganic chemistry is still an extremely young field, but it is tantalizing to envision that the recent developments made in directed evolution could potentially lead to innovative methods for the separations of REs.

Conclusions

Rare earths are arguably strategic resources (Fig. 4 and Box 2), as illustrated by global attention surrounding a 2010 supply crisis. Since that time, the market for REs has stabilized but is still heavily polarized. The reaction of most OECD (Organization for Economic Cooperation and Development) countries was to encourage research programs and/or form stockpiles. However, the recycling rates of REs from industrial scrap or "urban mines" are still extremely low. Solvent extraction is a mature technology and has many advantages regarding scalability, flexibility, automation, continuous operation, and targetable purities; it will likely remain the industry standard to separate complex RE mixtures from ore sources for the foreseeable future. The 2010 supply crisis provided several lessons. Restarting mining operation or large separation units is a risk for companies without a stable market. A clear need also exists for smaller-scale processes that target specific RE combinations from secondary sources. This Review describes chemistries that should contribute to this goal. A large share of the energy and materials consumed in the separation of REs lies in the mining and ore beneficiation to a concentrated, separable RE feed. Preconcentration of REs from scrap is similarly a challenge that has limited recycling schemes. Recent progress in the processing of scraps and selective extraction from other metals is promising (*68*, *69*) and indicates that a circular RE economy is on the horizon (*70*). Despite the challenges faced by Mendeleev and many others in the discovery and description of REs, their emergence and classification were a triumph of spectroscopy, quantum theory, and the periodic system of elements. Without doubt, these confounding elements will continue to provide surprises and opportunities for the progress of humankind.

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