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Devices and applications at the micro- and nanoscale

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PERSPECTIVE

Mine-on-a-chip: megascale opportunities for microfluidics in critical materials and minerals recovery

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The rising demand of mineral resources essential to the functionality of low-carbon energy technologies – critical minerals – and the security of their supply poses one of the most pressing bottlenecks toward energy sustainability. A suite of challenges arise, ranging from resource characterization to extraction and refining, that undergird the economic feasibilty and cradle-to-grave environmental compliance of decarbonization technologies. Myriad opportunities exist for the microfluidics community to engage, including materials characterization, mechanistic elucidation of extraction processes, chemical analyses, reagents screening, and separation device design, that leverage the distinct advantages of microfluidics, namely low sample and reagent requirements, ability to parallelize, and rapid and low cost testing. This perspective identifies key gaps and opportunities in securing the critical minerals supply, and aims to galvanize the LoC community in this critical research.

Minerals and their criticality to energy sustainability

Achieving the 2 °C climate target set in the Paris Agreement will require a ~ 10 to 100-fold growth in decarbonization technology deployment by mid-century.(1–4) Energy transition technologies such as wind, solar (photovoltaics and thermal), electric vehicles, hydrogen, and batteries, however, all rely critically on a set of mineral elements (e.g., lithium, cobalt, nickel, rare earth elements, platinum group metals, etc.) to enable their basic functionality (Fig. 1).(5) Increasing electrification and decarbonization of the global energy economy, therefore, imposes demand on this collective of elements – the so-called "critical minerals and materials" as defined by the U.S. Geologic Survey (USGS) and Department of Energy (DOE) – at unprecedented rates(6), whose reliable and cost-effective availability are essential to economic security and energy sustainability.(6–8)

Rapid growth in the demand of critical materials and minerals, however, leaves key vulnerabilities in decarbonization efforts as supply gaps emerge. For example, demand for Li, Ni, and Co are projected to increase between 20- and 40-fold by 2040 as a result of battery storage and electric vehicle adoption, yet supply growth from existing and planned mining operations, characterized by diminishing ore grades and long lead-times from discovery to first production (> 16 years), will be slow to follow.(9) The issue is exacerbated by the

This perspective calls the *Lab on a Chip (LoC)* community to develop solutions that help close the ever-growing gap in the critical minerals supply chain. Expanding and securing the supply of critical minerals, from exploration to refining, will require extensive materials characterization, mechanistic elucidation of microscale fluid-mineral interactions, analyses, screening, and separation – all capabilities inherent to microfluidics. In the following, we provide a description of the critical minerals, their uses, and criticality to energy sustainability, followed by a summary of their current extraction and processing and the challenges that exist therein. We highlight recent advances that the LoC community has contributed in response to the need for securing the critical minerals supply chain, and outline a set of "mine-on-a-chip" opportunities for which microfluidics techniques are well-suited.

geographic concentration of both resources and processing facilities, where trade dependencies effect price volatility and disrupt the economic feasibility of decarbonization technologies.(10) Current mining and processing practices are further weighed by their energy intensity and environmental emissions that challenge the economic feasibility of new production. While secondary streams such as waste recycling provides a pathway to reduce the demand for ore extraction, they remain unsatisfactory as a replacement in the nearterm (insufficient end-of-life material until 2040, when recycled Li, Ni, Co, and Cu from spent batteries can reduce primary supply by ~ 10%).(9,11) Continued mapping of new and unconventional critical mineral resources and their economic and ecologically-sound extraction and processing are therefore critical to ensuring a rapid and economically-viable energy transition.

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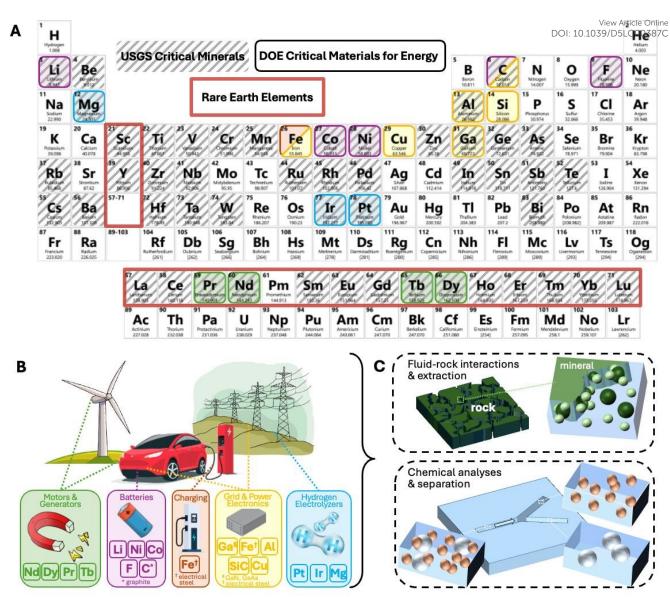


Figure 1 – Elements critical to energy sustainability, their uses, and opportunities for the Lab on a Chip community. (A) Critical materials and minerals highlighted on a periodic table. Critical minerals as defined by the USGS are denoted by diagonal hatching. Critical materials for energy (i.e., DOE's electric eighteen) are colored according to their uses in B. The rare earth elements (i.e., lanthanide series plus scandium and yttrium) are encircled in red. (B) The DOE's critical materials for energy as relevant to their uses in motors and generators for electric vehicles and wind turbines, batteries, charging infrastructure, grid and power electronics, and the hydrogen economy. (C) Opportunities for innovation using lab on a chip techniques in chemical analyses, separation, purification, extraction, and elucidation of fluid-rock interactions.

Critical materials and minerals definition

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The Energy Act of 2020 defines *critical materials* as "any non-fuel mineral, element, substance, or material that ... (i) has high risk for supply chain disruption; and (ii) serves an essential function in one or more energy technologies, including technologies that produce, transmit, store, and conserve energy" identified by the U.S. Department of Energy, and *critical minerals* as "any mineral, element, substance, or material designated as critical" by the U.S. Geological Survey.(12)

The 2023 DOE Critical Materials Assessment (CMA) identified 18 elements (e.g., Li, Nd) and material composites (e.g., silicon carbide, electrical steel) crucial to energy sustainability in the immediate and medium-term (through 2035, Fig. 1A, colored and Fig. 1B): aluminum

(Al), cobalt (Co), copper (Cu), dysprosium (Dy), electrical steel (Si-Fe), fluorine (F), gallium (Ga), iridium (Ir), lithium (Li), magnesium (Mg), natural graphite (C), neodymium (Nd), nickel (Ni), platinum (Pt), praseodymium (Pr), terbium (Tb), silicon (Si), and silicon carbide (SiC).(13) These 18 materials, the "electric eighteen", are of particular criticality due to their importance to energy and vulnerability to supply risk (Fig. 2). In the CMA, material importance to energy is defined by the market use of a material in existing and future energy technologies as well its capacity for substitution.(13) Supply risk is evaluated by the capacity for global supply to meet demand based on technology growth trajectories for deployment scenarios(14,15), competition from non-energy sectors, geographic market concentration, co-dependence of precious minor elements

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on lower-value products, and social and political factors including regulatory, labor, and export restrictions.(13)

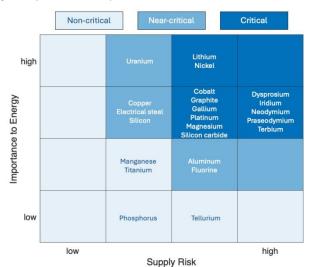


Figure 2 – Set of materials that are critical to the energy sector in the immediate- and medium-term (2025 to 2035) according to the U.S. Department of Energy 2023 Critical Minerals Assessment.(13)

The 2022 USGS list of critical minerals comprises 50 elements and crystallographic compounds (e.g., barite, fluorspar) important to economic or national security (Fig. 1A, hatched): aluminum (Al), antimony (Sb), arsenic (As), barite (BaSO₄), beryllium (Be), bismuth (Bi), cerium (Ce), cesium (Cs), chromium (Cr), cobalt (Co), dysprosium (Dy), erbium (Er), europium (Eu), fluorspar (CaF2), gadolinium (Gd), gallium (Ga), germanium (Ge), graphite (C), hafnium (Hf), holmium (Ho), indium (In), iridium (Ir), lanthanum (La), lithium (Li), lutetium (Lu), magnesium (Mg), manganese (Mn), neodymium (Nd), nickel (Ni), niobium (Nb), palladium (Pd), platinum (Pt), praseodymium (Pr), rhodium (Rh), rubidium (Rb), ruthenium (Ru), samarium (Sm), scandium (Sc), tantalum (Ta), tellurium (Te), terbium (Tb), thulium (Th), tin (Sn), titanium (Ti), tungsten (W), vanadium (V), ytterbium (Yb), yttrium (Y), zinc (Zn), and zirconium (Zr). Although the broader list of 50 minerals identified by the USGS are essential to the economic and national security of the U.S.(16), this perspective will focus on the DOE's list of energy-critical materials (i.e., the "electric eighteen"). Importantly, we note that the criticality of elements to the energy economy is fluid and evolves with developments in supply and technology such that currently near- and non-critical materials may become critical in time.

Rising demand for critical materials

For the electric eighteen, material criticality is driven primarily by recent and projected use surges in electric vehicles, battery storage, hydrogen electrolyzers, efficient lighting, power electronics, and grid infrastructure.(13) Adoption of electric vehicles rose ~ 15-fold from 2015 to 2022(13), and is projected to grow ~ 30-fold by 2040.(9) These unprecedented rates of EV technology adoption engenders criticality in the minerals essential to battery storage (Li, Co, natural graphite, Fig. 3), high-grade permanent magnets used in electric motors (Nd, Dy, Pr, Tb, Fig. 3), motor and charging infrastructure (electrical steel), and power electronics (SiC, GaN). Specifically, lithium-ion batteries leverage the small size and large charge density

of lithium - suitable for reversible intercalation in electrodes to enable rechargeable electrical energy storage 🗀 ବ୍ୟବ୍ୟ ନୃତ୍ୟ ପ୍ରଥମ dense storage. Cobalt, nickel, and graphite electrodes are used commonly to maximize the energy storage density of Li-ion batteries. Consumption of battery electrolytes such as lithium hexafluorophosphate and polyvinylidene fluoride will increase accordingly, raising demand for fluorine. Although next-generation battery chemistries targeting Earth-abundant materials may reduce the material intensity and criticality of lithium and cobalt, market momentum for current low-cost technologies remain. Together with grid-scale battery storage, demand for lithium by the EV sector is anticipated to increase ~ 40x by 2040, double the supply from existing mines and planned projects, and demand for graphite, cobalt, and nickel are expected to grow ~ 20- to 25-fold.

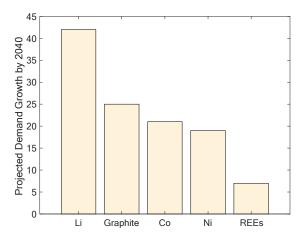


Figure 3 – Projected demand growth of critical minerals used in batteries, electric vehicles, and wind turbines. Data from EIA report.(6)

A second set of minerals essential to the function of electric vehicles are the rare earth elements. Specifically, EVs rely on permanent magnets in their motors to convert between electrical and mechanical energy.(17) Demand for lightweight, compact, and highgrade magnets – the most economic of which are neodymium-ironboron (NdFeB) magnets - is a key driver of the REEs toward criticality.(17-19) Here, the rare earth elements, including neodymium, dysprosium, praseodymium, and terbium, are leveraged for their large magnetic momentum, given by their unique electronic configurations where electrons occupy their 4f orbitals partially. The functional criticality of REEs in permanent magnets, therefore, ties their demand closely to the adoption of EVs, the sales of which increased ~ 35% year-on-year between 2023 and 2024.(20) While the development of REE-free magnets promise to reduce the criticality of REEs, their functionality relies on other critical minerals such as Pt, Ni, and Co.(21,22) Sustained market share growth – even at business-as-usual rates - is expected to generate supply gaps in the REEs that undermine the economic feasibility of low-carbon energy technologies (Fig. 4).

Elsewhere, growth in renewable electricity generation is also key driver in mineral criticality. Off-shore wind capacity is anticipated to increase 5- to 7-fold by 2035(23), furthering demand for rare earth magnets that are essential to the function of its generators. Dysprosium is particularly important to resist demagnetization over

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long periods of performance.(17) Similarly, power production from solar photovoltaics grew 25% from 2022 to 2023(24), imposing stress on the supply of silicon semiconductor materials. Specifically, crystalline silicon (Si) remains the most widely-used and costcompelling semiconductor material for photovoltaics, while newer solar cell arrays leverage gallium nitride (GaN) for its wide bandgap with low sensitivity to ionization radiation.

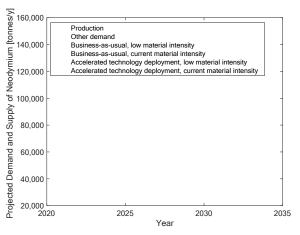


Figure 4 - Growing gap between global demand and production of neodymium. Four demand scenarios are considered here as a function of market penetration and material intensity of technology. Modified from the U.S. Department of Energy 2023 Critical Minerals Assessment.(13)

To ensure grid security, power generation from intermittent energy resources (e.g., wind, solar) drives the growth of grid-scale storage technologies. Battery storage is anticipated to grow ~ 40-fold by 2030(13), with demand in Li, Ni, and graphite resources to follow. In addition to batteries, non-electric materials suitable for longduration energy storage such as hydrogen will be required to compensate for daily and seasonal fluctuations. Growth in the production of green hydrogen (i.e., H2 reduced from water using proton exchange membrane, PEM, electrolyzers) will drive increases in demand for stable electrolytic catalysts. Here, platinum and iridium, members of the platinum group elements (PGEs), are critical to catalyze water electrolysis.(13) Specifically, Pt and Ir hold excellent chemical stability in extreme aqueous environments and catalyze the oxygen- and hydrogen-evolving reactions during water electrolysis, respectively.(8) Magnesium, similarly, provides high energy density and excellent electrochemical properties that enable its application in next-generation battery and H2 electrolyzer technology.

Lastly, to accommodate increased electrification, sustained growth in power electronics and in the power grid market (~ 150% increase by 2032(13)) will stress existing supplies of silicon carbide (SiC), gallium nitride (GaN) and arsenide (GaAs), electrical steel, copper, and aluminum. Major conductor elements such as aluminum, copper, and electrical steel provide critical function in the electrical infrastructure, from power lines to motors.

Overall, demand for the "electric eighteen" are projected to increase at unprecedented rates, the secure supply of which is critical to a sustainable energy future. The global aggregate market value of lithium, nickel, cobalt, copper, graphite, and the rare earth elements was ~ \$325 billion USD in 2023, and is expected to 914 Pred Se to 60 \$770 billion USD by 2040.(14) Yet, key vulnerabilities exist in their supply as a result of the heterogeneity of natural resources, their energyand emissions-intensive production, and potential geopolitical barriers. In the following, we discuss these challenges and outline opportunities for the LoC community to participate.

The problem with minerals supply

Reliable supply of the critical minerals above provides the necessary foundation for a timely and cost-feasible energy transition. Gaps in supply create market vulnerabilities that undermine the pace, price, and scale at which decarbonization technology can be deployed. Key stressors to the global supply of minerals include geographic concentration of resources and processing capabilities, timescales associated with mine development, declining resource quality, and concerns over environmental and social implications of mining practices.(9) Here, we discuss the challenges associated with critical minerals sourcing, and outline horizons for how microfluidics can help to broaden the supply through unconventional resource characterization and materials extraction and separation.

Mineral resources: occurrence and alternatives

Global occurrence of energy-critical minerals is nonuniform, with mining operations concentrated geographically in a small number of countries. As an example, we highlight here the geographic concentration of both the resource base and processing capabilities of the rare earth elements.

Unlike their name suggests, the rare earth elements (REEs) occur ubiquitously in the Earth's crust. Concentrated deposits of economic value, however, are scarce. Current economic accumulations of the rare earth elements are hosted in and mined primarily from magmatic deposits and weathered clays in China (Fig. 5, ~ 50 and 70% production of global and 2024. reserves in respectively).(17,18,25,26) While the REEs typically occur together, the mineral ores such carbonatite (> 50 % calcite and/or dolomite), monazite ((REE,Th)PO₄) and apatite ((Ca,REE)₅(PO₄)₃(F,Cl,OH)) tend to be enriched in the light REEs (LREEs, from La to Eu). The heavy REEs (HREEs, from Gd to Lu, and Y, Sc), on the other hand, accumulate at elevated concentrations in weathered clay systems.

The principal commercial source of the LREEs is carbonatitic ore, an igneous rock crystallized from CO2-rich fluids.(27) Typically, carbonatitic deposits are enriched in the light REEs with few HREEs (e.g., Dy, Tb) as a result of fractional crystallization.(27-30) Here, enrichment is enabled via hydrothermal convection in continental rift settings, where REEs in deep mantle melts - whose large ionic radii are incompatible with the crystal lattices of most rock-forming minerals - are excluded, remain in solution, and precipitate as REEenriched phases.(17,29,30) Specifically, the nuclear charges of the REEs are shielded weakly by their 4f electrons, and result in decreasing ionic radii with atomic number (i.e., the so-called "lanthanide contraction"). As a result, the smaller HREEs cations are incorporated more readily in rock-forming minerals in the Earth's crust, while the larger LHREEs remain in solution.(27,28,31) The

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higher solubility of the LHREEs in hydrothermal fluids leads ultimately to the precipitation of mineral ores that are enriched in LREEs, including carbonatites. Of the four major carbonatitic mines in operation, three are in China – Bayan Obo (~ 4 to 6 wt.% rare earth oxides, REOs), Maoniuping (~ 2 wt.% REOs), and Dalucao (~ 2 wt.% REOs) – and one in the U.S. (Mountain Pass, California, ~ 8 wt.%

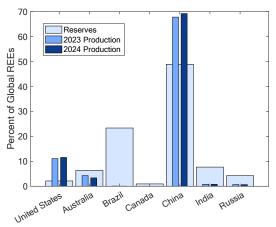


Figure 5 – Concentration of global REEs occurrence and production capacity in a few countries. Resources and extraction are dominated by China. Nonuniform geographic distribution of supply presents vulnerabilities in the reliability and availability of raw material resources needed for sustainable energy technologies. Data from USGS Minerals Commodities Report 2025.(10)

REOs).(17,32)

The HREEs including Dy and Tb, on the other hand, are extracted primarily from weathered ion-adsorption clays of Southern China.(33-38) Primary mineral phases that hold elevated concentrations of REEs include kaolinite, where REEs are adsorbed weakly on basal surfaces.(39) Enrichment of the HREEs in clays follows the supergene process. Specifically, in the warm and humid subtropics, REEs held in granitic and tuff minerals are released via weathering and carried by meteoric water into the clays below (i.e., supergene enrichment).(33-35) Heavy rainfall in temperate climates further enhances supergene enrichment by removing the overlying REE-depleted material and enabling continuous REEs enrichment in the clays (~ 500 to 2000 ppm).(39-43) Although REE concentrations in clay deposits are low compared to those of primary igneous ores, commercial mining from clays is feasible owing to their HREE concentration, high surface area to volume ratio, ease of mining, and weak REE attachment.(39,44-48)

Beyond the REEs, other energy-critical materials experience similar geographic concentration in resources and extraction. Cobalt deposits are concentrated principally in the Democratic Republic of Congo (DRC), which, as of 2024, held $^{\sim}$ 55 % of global reserves and contributed $^{\sim}$ 76 % of production (Fig. 6). For lithium, over 50 % of global reserves and production in 2024 were controlled by Chile and China. The challenges with geographic concentration extend beyond those of resource heterogeneity and extractive operations; concentration of refining capabilities is similarly acute, with $^{\sim}$ 85 to 90 % of all refined REEs and $^{\sim}$ 50 to 70 % of lithium and cobalt on the market originating from China. The geographic concentration of raw mineral resources, their mining, and refining lead to global

interdependencies on trade and policy, and introduces key vulnerabilities in the price and reliability of the learn material

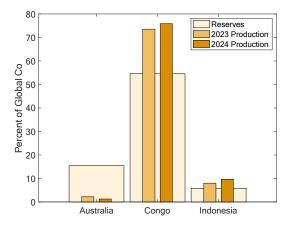


Figure 6 – Concentration of global REEs occurrence and production capacity in a few countries. Resources and extraction are dominated by China. Nonuniform geographic distribution of supply presents vulnerabilities in the reliability and availability of raw material resources needed for sustainable energy technologies. Data from USGS Minerals Commodities Report 2025.(10)

resources needed for decarbonization.

Democratizing the supply of critical material resources will require broadening of existing supplies to include unconventional and secondary resources such as lower-grade natural deposits(49), industrial and mine wastes(49–52), and end-of-life devices (i.e., electronic wastes).(11) Legacy coal ash, for example, are fine particulate residues from centuries of coal combustion around the world that hold elevated concentrations of the rare earth elements (up to 1500 ppm reported).(52–56) U.S. stockpiles of coal ash are estimated around $^{\sim}$ 5.3 gigatons (1.5×10¹² kg)(52) and collected primarily in unlined landfills and ponds adjacent to coal-fired power plants that leak contaminants to local ecosystems. Extracting REEs from these legacy waste piles hence provides an exciting horizon to valorize while remediating legacy ash piles simultaneously.(49)

Much remains unknown, however, of the physicochemical characteristics of these materials - often with high degrees of heterogeneity and complexity – and their conduciveness to minerals REEs extraction from coal ash, for example, is extraction. complicated by regional variations in composition and inadequate descriptions of their material properties that limit current state-ofthe-art recovery to only ~ 15%. As a result, coal ash is currently considered an abundant yet non-economic resource. To leverage unconventional resources, deposit mapping and the development of economically-viable extraction approaches from them will require extensive sets of spatial and chemical analyses. Historically, material characterization of low-grade ore and industrial wastes has been sparse as a result of their low economic value. Here, to compensate for the lower resource grade of unconventional supplies, approaches that are inexpensive, rapid, and amenable to large sets of experiments - unique capabilities of microfluidics - will be particularly sought-after.

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Extraction: economic and environmental costs

Additional vulnerabilities in meeting the ever-growing demand for critical materials are marked by the economic and environmental costs associated with mining, extraction, and processing. Myriad challenges exist, from the depletion of existing ore, diminishing ore quality, and lead-times for new mine developments, to the ecological impacts of mining and extraction, environmental emissions, and competition for strained resources (e.g., water). Technology growth has driven mining of high-grade ore, where costs associated with extraction and processing are minimal. Resource exploitation, however, has depleted easy-to-access and easy-to-process deposits, leading to growing importance of lower-grade accumulations. Copper ore grades in Chile, for example, have decreased ~ 30% over the past 15 years.(9) Mining, extraction, and processing of deposits with low CMs concentrations, however, are associated with higher energy and economic costs as well as environmental emissions (CO₂, tailing wastes, spent reagents, etc.).

To compensate for the growing gap between demand and declining ore quality, new mines will need to be developed. On average, mining projects require ~ 16 years from discovery to first production.(57) These timescales far exceed those necessary to sustain the energy transition. Here, opportunities exist for leveraging unconventional and secondary resources such as mine and other industrial wastes, as well as co-production of critical minerals (e.g., REEs) from existing mining operations.

Once mined, mineral ores undergo a series of processes to extract, separate, purify, and refine into commercial products (e.g., rare earth oxides, lithium carbonate, etc.).(58) Each step is energyand reagent-intensive, generating large volumes of wastes that impact economic and ecological viability. Economic extraction of REEs from high-grade bastnäsite ore, for example, relies on high temperature roasting (e.g., 500 °C) that decomposes the carbonate mineral to minimize acid consumption. (59,60) On average, each ton of rare earth elements produced from these high-grade carbonatites generates ~ 8.5 kg of fluorine, 13 kg of flue dust, and 9600 to 12,000 m³ of hydrofluoric acid (HF), sulfur dioxide (SO₂), and sulfuric acid (H_2SO_4) of gas emissions, ~ 75 m³ of acidic waste water, and ~ 1 ton of radioactive waste residues (thorium, uranium, etc.).(61,62) Similarly, REEs extraction from monazite emits 65.4 kg CO₂e/kg of greenhouse gases, and consumes ~ 11,170 kg/kg of water and ~ 917 MJ/kg of energy.(63) Water stress, particularly in arid regions (e.g., Inner Mongolia), pose additional challenges on the sustainability of minerals mining. Likewise, production of the heavy REEs from supergene clays via in situ ammonium sulfate ((NH₄)₂SO₄) leaching emits 258 to 408 kg CO₂e and consumes 270 to 443 MJ primary energy per kg of mixed HREOs, all the while altering the local soil geochemistry.(64) Extraction processes that limit the ecologic footprints of both open pit LREE mining and in situ HREE leaching are sought urgently.

In addition to reducing the ecologic footprint of CMs extraction from conventional ores, securing CMs supply will also require economic and environmental recovery from lower-grade unconventional resources. Secondary resources and wastes such as coal ash, excitingly, hold potential to expand REEs production ~ 7- to

8-fold.(52) Current extraction approaches, however will extract extraction and energy-intensive and limit the market will extract extraction of the ex

Many questions remain around the reaction pathways and kinetics, secondary processes, and reagent chemistry that are necessary to design CMs extraction approaches that are both effective and cost-efficient. Fundamental understanding of the geochemical characteristics of feedstock materials, including coupled reaction and mass transfer processes in the beneficiated media and the screening of reagents for high-yield extraction, are needed. Capabilities to visualize the multiphase reagent transport through beneficiated ore and unconventional materials provide a means for direct observation of extraction processes in porous and/or granular resource beds. Fundamental geochemical interactions between reagents and the resource must be understood to engineer green chemistry approaches for accelerating CMs extraction. Similarly, processes to minimize and recycle reagent wastes are needed to reduce the ecologic impacts and to increase the economic viability of alternative extraction approaches.

Separation

Once the CMs are extracted from feedstock material (ore, industrial wastes, etc.), they need to be separated and purified prior to market use. Typically, the CMs occur together with secondary species that are co-extracted. Physicochemcial similarities between the CMs and the associated cations render their separation difficult.

In salar brines, for example, lithium (~ 100 to 1000 ppm) is associated commonly with major cations that are difficult to separate from (e.g., ~ 10 wt.% Na, K, Ca, and Mg).(68,69) Currently, the production of a relatively pure Li product (e.g., > 99 % purity Li₂CO₃, LiOH) separates Li from secondary cations via a sequence of precipitative and fractionative processes that are slow (~ 24 months) and lossy (~ 30 to 50 % loss during evaporative precipitation).(70) Selectivity of Li from magnesium, for example, is particularly challenging due to the physicochemical similarities between the two hydrated species. Specifically, Li and Mg hold similar hydrated ionic radii (3.8 Å for Li, 4.3 Å for Mg²⁺).(71) Recent advances include the use of solvent extraction, sorbents (e.g., aluminum-, titanium-, manganese-based spinels), membranes, and electrodialysis to separate Li from dissolved Mg²⁺, but are challenged with costly reagent and energy requirements.(72) Favorably, the effectiveness and cost-feasibility of separation technologies improve with Li enrichment (i.e., Li/Mg, Li/Na, Li/Ca, Li/K ratios). Solutions that enable the enrichment of Li in brines, therefore, will provide an important opportunity to enable the market feasibility of Li separation technologies. Similarly, solutions that enable the

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separation of Li from low-grade resources (e.g., oil and gas produced waters)(73) are also needed to broaden the supply of Li.

Separation of the rare earth elements, on the other hand, are complicated by their tendency to occur together, their association with major cations that are far more abundant (e.g., Ca, Al, Fe, etc.), and their co-existence with radionuclides (up to \sim 20 wt.% thorium and uranium oxides in monazite).(17,18) Physicochemical similarities between the REEs, namely their trivalent charge and ionic radii, lend to their co-occurrence in nature.(74) crystallization of principal rock-forming minerals (e.g., silicates) favors the incorporation of cations with valences of 2 or 1 and excludes the REE3+ cations, enabling the formation of REE-enriched ore that contain the entire lanthanide series.(17) Purified individual rare earth metals or oxides production, therefore, requires selectivity based on subtle differences in ionic size and charge.

Approaches to separate the individual rare earth elements include fractional crystallization (i.e., selective precipitation), redox, ion exchange, and solvent extraction.(32,75–79) crystallization, for example, is used to precipitate the heavy REEs from ion-adsorption clays as oxalate salts.(80) Here, rare earth oxalates precipitate except at very low pH while major cations (e.g., alkalis and alkali earths) remain soluble.(80) Selectivity from transition metals and radionuclides, however, is limited by coprecipitation, while separation between the individual REEs require many stages of precipitation and dissolution owing to the low solubility product and water solubility of REE salts.(80-82) As a result, selective precipitative processes consume extensive volumes of reagents that raise the economic and environmental costs of separation. Ligand-based approaches such as ion exchange and solvent extraction face similar challenges in the competitive complexation of REEs and secondary species for binding sites and its reagent use.

Techniques to purify and separate critical minerals from their associated species are needed to produce market-ready CM streams. For example, economic approaches that enhance the subtle physicochemical differences between the individual CM elements provide an avenue toward enabling the market viability of production from lower-grade ore and unconventional resources. Understanding of the coupled reaction kinetics, thermodynamics, and mass transfer associated with multiphase fluid flow in low Reynolds number environments will be particularly important in designing and optimizing efficient separation systems. Method development, including ligand design, flow configuration, and reactor conditions will require screening techniques amenable to large sets of experimental conditions.

Megascale opportunities in microfluidics

An exciting set of opportunities exist for the LoC community to help in securing the supply of critical minerals, from microfluidic flow devices that help to purify and separate the CMs, to geochemical micromodels that lend insights on extraction and reagent design. While polymer-based LoC technologies designed for biological compatibility are limited in applicability for the harsh temperature, pressures, and fluid compositions (pH, salinity) necessary for CMs extraction and processing, advances in "hard" microfluidics (e.g.,

glass, silicon, rock)(83-92) provide an avenue to leverage LoC techniques to help secure critical minerally supply. 9/DBelow, 38We highlight a set of opportunities for microfluidics, along with recent advances by the LoC community.

Microfluidics

The compositional heterogeneity and complexity of solutions bearing critical materials (e.g., produced brines from oil and gas or geothermal wells) requires the design of customized reagents (ligands, solvents, etc.) and processing conditions (e.g., pressure, temperature, pH, flow rates) to optimize their extraction and separation. Techniques amenable to rapid, inexpensive, and massively-parallelizable screening are needed.

Microfluidic approaches, well-suited to the design, screening, and manipulation of microscale fluids and colloidal systems, are particularly amenable to the purification, and separation of CMs owing to their small sample requirements, high throughput, rapid analyses, and multiplexing capabilities.(93) For example, dissolved species in homogeneous (i.e., single phase) solutions can be separated using field-flow fractionation methods that leverage cross fields (e.g., electric, magnetic, etc.) to induce and/or enhance the spreading of solutes.(94) Charge- and size-based solute separation in single-phase fluids are likewise enabled via electro-osmotic flow (EOF), where bulk flow is induced in response to interactions between the charged species and the electric double layer at wall surfaces. Bottenus et al(95) demonstrated rapid (< 10 min) EOFbased separation of the REEs (La through Pm), for example, by leveraging the increased surface area-to-volume ratio of a fusedsilica microchannel. Approaches that separate ionic species without the use of external input (e.g., heat, electric fields, ligands, etc.) have also been sought. Recently, Wang et al developed a laminar co-flow platform that separates Mg from Ca by maintaining a reactive interface with steep concentration gradients.(96) Research in the development and use of microfluidics for CMs separation is in its early stages and is ripe with opportunities.

In two-phase fluid systems (e.g., liquid-gas, liquid-liquid), interfacial hydrodynamics and thermodynamics can be leveraged to further improve the separation of dissolved species. Importantly, transport is enhanced in microfluidic platforms, where capillarity enables passive flow. Recent advances include a thread-based device by Quero et al(97) that leverages capillary electrophoresis to separate Li from K and Na, and a fiber-based microfluidic approach to crystallize lithium away from sodium by Chen et al(98). Here, capillarity is leveraged to enhance the differential charges, solubilities, and diffusivities of the salts. Paper-based approaches used widely in biological sciences provide similar advantages in costand time-effective separation, yet its application in critical minerals is relatively unexplored.

In solvent extraction, the development of ligand species that facilitate the partitioning of CMs species out of aqueous solutions will require rapid analyses and screening. Microfluidics are particularly amenable to this given it small diffusion lengths, high surface areato-volume ratios, tight residence time distributions, and precise flow configurations. Microfluidic channel reactors, for example, enable rapid mass transfer across their narrow cross-sections, the PERSPECTIVE Lab on a Chip

parallelization of which allows for high throughput (up to 1 L/h) solvent extraction.(99) Similarly, droplet microreactors generate colloids with precision, which enables rapid screening of solvent compositions. Fernández-Maza et al optimized the separation of Dy from La for a range of solvents, ligands, and aqueous phase pHs.(100) Microfluidics are primed to help understand and optimize CMs separation, particularly aqueous species such as Li and Mg, and present a set of exciting opportunities for the LoC community to engage.

Geochemical microfluidics

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The extraction of CMs, whether from conventional or secondary resources, will require understanding and optimization of the coupled reactive transport processes at fluid-solid interfaces. Here, many questions remain open, including the transport of multiphase fluids through porous or granular media, wetted reactive surfaces, coupling between transport and reactions, and the interplay between ionic species on extraction kinetics.

Microfluidic platforms that mimic the morphology of porous or granular media – micromodels – enable the direct observation of wetting and multiphase flow phenomena through complex porous geometries.(101–104) Flow configurations through resource materials, for example, determines the overall recovery rate of the embedded critical minerals. In porous/granular media, pore size heterogeneity leads to preferential flow paths where reagent delivery and residence times are nonuniform and the overall recovery rates are reduced significantly.(105,106) Further, heap and in situ leaching processes where aqueous reagents share pore space with air are dominated by multiphase flow characteristics.(106) Micromodels that replicate the pore geometry of CM-bearing resources provide insights into approaches to maximize the access of reagents to the pore space and the so-called "sweep efficiency".

Extraction of critical minerals from their hosting matrices ultimately relies on the chemical interactions between fluids and mineral surfaces, and require probes that honor mineral chemistry. Geochemical microfluidics marry the advantages of microfluidics with the mineral reactivity of geologic and geologically-derived material resources.(83-87,107) Notably, geochemical micromodels resolve the interplay between reactions and multiphase transport at fluid-mineral interfaces to understand the spatiotemporal associations of fluid phases, dissolved species, and interfacial reactions. For example, Gerardo et al resolved the reactive transport mechanisms controlling REEs leaching from coal ash to design lowreagent approaches for recovery from secondary wastes. (55,108) Interweaving the geochemistry of mineral-bearing resources with direct microscale visualization enables the cost- and time-effective screening of reagents as well as the understanding of fundamental reaction couplings at the pore/granular level.

Similarly, ore beneficiation often results in a distribution of grain sizes, including sub-micrometer particles (i.e., "fines"). Fine particulates are prone to mobilization with changes to solution composition (e.g., cation speciation, concentrations, pH, temperature), the redeposition of which result in flow path obstruction (i.e., formation damage) and the reduction of reagent access. Extractive processes that dissolve bulk minerals also

contribute to dislodging fines, exacerbating their migration and impacting the accessibility of reagents to the example, provide a means for exploring these effects. (85,86)

Finally, elucidating fundamental reaction processes at mineral surfaces will require nanoscale resolution. Recent advances in nanofluidics enable the spatiotemporal resolution of dynamic fluid-solid interactions, including *operando* scanning electron microscopy devices(88), allows the study and design of fundamental coupled reactive transport processes underlying CMs extraction at the interfacial- and molecular-levels. The ability to capture simultaneously the multiphase fluid dynamics and reaction within the porous/granular fluid-mineral interfaces in CM-bearing resources enables the determination, design, and optimization of their extraction viability, critical to the security of CMs supply.

Overall, micro/nanofluidic resolution of coupled reactions and transport at fluid-mineral interfaces provide a fast and inexpensive approach to screen for reagent compositions, flow rates, and operation temperatures/pressures that optimize upscaled extraction operations such as those in heap leaching and hydrometallurgy. The mineralogic heterogeneities encountered in metals-bearing resources (e.g., ore, industrial wastes, etc. that hold REEs, Co/Ni, Cu, PGEs) introduce a complex set of interfacial geochemical interactions that are not easily modeled. Spatial resolution of mineral phase distributions and their accessibility by reagents (e.g., abutting pores or fractures) enabled by microfluidics, excitingly, allow for fundamental understanding and modeling of the upscaled hydrometallurgical operation.

Conclusions

Ready availability of the elements critical to energy decarbonization, the so-called "critical minerals and materials", are of increasing importance and urgence. Challenges arise from geographic concentration of the resources to their energy- and reagentintensive processing. State-of-the-art approaches in the mining sector, particularly the rare earth elements, rely on ecologically- and economically-costly hydrometallurgical approaches that render the domestic supply chain vulnerable to instability. Here, opportunities abound for the LoC community to assess unconventional resources and to develop new extraction approaches that are better aligned with the sustainability goals of low-carbon energy technologies. In particular, the small volumes, high throughput, and multiplexing capabilities of microfluidics are well-suited to provide rapid characterization of material properties to aid with prospecting and to determine their physicochemical conduciveness to extraction. Likewise, characterization of the fundamental reactive transport processes that extract CMs from their granular host rock, including reagents screening to achieve low environmental impacts extraction, are well-suited for geochemical micromodel studies. While the two communities have been isolated in the past, longstanding expertise in microfluidics to probe and control coupled flow and reaction through miniature, massively-parallelized systems is well-suited to prospect, screen, and optimize critical materials supply. Likewise,

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the intersection of critical materials and minerals with micro/nanofluidics provides an exciting new frontier for the LoC community to tackle.

Conflicts of interest

There are no conflicts to declare.

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Data availability statement:

All data used in this article have been included in the cited works.