U.S. Department of Energy

Advanced Research Projects Agency – Energy (ARPA-E)

Request for Information (RFI)

DE-FOA-0002751

on

Phytomining for carbon-negative critical mineral supply chains

Introduction

The purpose of this RFI is to solicit input for a potential future ARPA-E research program focused on technologies related to harvesting high value metals essential for the clean energy transition from terrestrial environments using metal hyperaccumulators (HAs). The goal is to establish economic, sustainable, and low carbon-footprint domestic supply chains of high value metals to promote an accelerated clean energy transition without supply chain constraints. ARPA-E is seeking information at this time regarding transformative and implementable technologies that could:

(a) Identify or develop hyperaccumulators suitable for economically viable phytomining in the United States. Examples include agronomic techniques to domesticate hyperaccumulating species, yield higher biomass, and to control the seed dispersal; systems biology approaches to gain desired phenotypes such as high rates of growth, fast metal uptake, and accumulation of optimal metal compounds in parts of the plant that are optimal for extraction with low carbon-footprint approaches. ARPA-E's interest includes perennial species with high biomass and high metal uptake, including tree species, and any hyperaccumulators that could be grown on high-metal, nonarable lands in the US such as ultramafic serpentine soil and mine tailings.

(b) Increase total metal uptake in hyperaccumulators that can be grown at large commercial scales in the United States. Examples include microbiome engineering to dissolve metals and engineering hyperaccumulators to grow deeper roots to expand the pool of metals available without strip mining. System-level approaches are encouraged to address the questions in this RFI. For example, employing integrated rhizosphere engineering, metal transport, and accumulation to desired locations in the plants such as saps, accumulation of metals in desired chemical forms, and monitoring/analysis tools.

(c) Extract metal from hyperaccumulators using processes that produce the lowest possible carbon emissions, ideally even carbon-negative. Examples include pre-treatment of biomass before or after drying to increase the yield, new metallurgical routes to extract metals with high yields and low impurities, and novel approaches to extract metals in desired chemical forms. ARPA-E is seeking information regarding extraction strategies without emitting carbon accumulated in the biomass back into the atmosphere. System-level approaches are encouraged to address the questions in this RFI. For example, employing integrated treatment of biomass to utilize accumulated carbon while extracting metals, co-processing of more than one type of biomass, integration with existing biomass processing routes, and recycling and recovery towards circular processes and economy.

(d) Produce high-value, high-purity chemical forms of metals directly from phytomining, which can enter the value chain of battery manufacturing and other clean-energy technologies without further processing. ARPA-E is seeking information for shortening the routes to clean energy-relevant mineral forms that can be used with minimal additional cost (CAPEX, energy, processing).

Note that some approaches may fit several of the technology categories described above. For instance, systems biology optimization of hyperaccumulators could be used to develop hyperaccumulators that are suitable for the climate and soil in the United States, while also increasing biomass, increasing metal uptake, and yielding the desired physical or chemical form of the metals of interest. Using nickel as an example target metal, ARPA-E is seeking information for new approaches that could reach at least 500 kg Ni/ha per year and >90% net greenhouse gas reduction compared to the state-of-the-art HPAL (high pressure acid leaching) process based on a lifecycle analysis.

Mining and Processing for a fully U.S.-based critical mineral supply chain

A number of minerals have been identified as vital to the continued existence of technology and civilization[1], and are therefore a national security and economic concern. For nearly a century, the United States has struggled to create an adequate domestic supply of these critical minerals. As progress toward electrification is recognized, the difficulty of securing an appropriate domestic supply of these minerals for United States energy supply and security has been highlighted. The domestic supply of essential minerals produced by conventional mining operations in the United States is insufficient to meet the accelerated need for full electrification in the United States, and an alternative domestic supply of these minerals could increase energy security for the clean energy transition.

To secure a fully U.S.-based supply chain for critical minerals, sustainable and economic extraction and processing are required. However, due to the comminution required to process ore, traditional mining processes are among the most energy-intensive industrial processes. For clean energy-critical minerals, the ore quality currently accessible in the United States is poor, and the energy required for comminution increases as the ore quality decreases. Nickel, for example, has often been extracted from sulfide ores rather than laterite. While laterite has a larger nickel content than sulfide, it is more difficult to process for nickel extraction, necessitating high pressure and temperature acid leaching, and is thus less commonly utilized due to the high CAPEX involved[2].

Geological processes have resulted in heterogeneity of metal concentrations in the Earth's crust, such that concentrated ores are found in certain nations based on their geologic history. For instance, nickel and cobalt ores can be found in countries with weathered ultramafic (metal-rich) rock, such as New Caledonia and Indonesia. Rare earth element (REE) deposits can be found in areas with carbonate-rich igneous rocks (USA, China) and clay deposits that have accumulated sorbed rare earth elements (China). However, all elements are found at lower (background) amounts in all continental crusts, in all countries. As a result, "unlocking" the comparatively low concentrations of key minerals in surface soils and surface rock by concentrating them to economically feasible concentrations in hyperaccumulator

[1] United States' Critical Minerals Stockpiling Act, 1939.

[2] Mudd, Gavin, Nickel Sulfide Versus Laterite: The Hard Sustainability Challenge Remains. Canadian Metallurgical Society, 2009.

biomass may ensure localized and secure metal sources. Currently, processing capacity (CAPEX investments) is concentrated in a few regions, such as REE processing capacity in China, and nickel processing capacity in Indonesia, where unprocessed ores are sent for refining. If low-energy and low-CAPEX processes could be co-designed with hyperaccumulators, phytomining may secure a fully U.S.-based supply chain for critical minerals, from source to processing to the end-use customer.

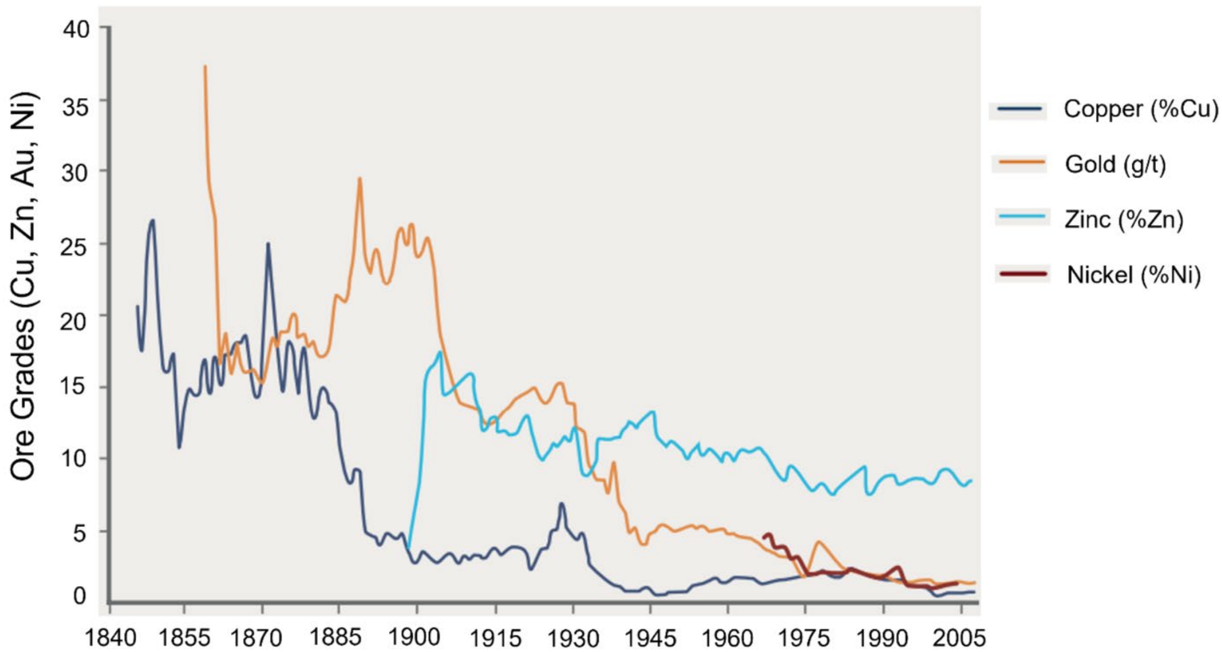

Figure 1: Grades of copper, gold, zinc, and nickel ore mined are decreasing over time[3].

Critical minerals are typically obtained from large-scale terrestrial mining operations. The concentrations of the critical minerals are often a few percent to a fraction of a percent by mass, necessitating not only extensive separation and purification processes in addition to mining processes, but also a considerable amount of material waste per tonne of mineral. These low-concentration minerals are also very expensive to mine, and ore grades are decreasing over time, as the most economical (most concentrated) ores are mined first (Figure 1). Aside from the high expense of obtaining critical minerals in the United States, processing, isolating, and purifying the metals in the traditional manner is also costly. Avalon Rare Metals, for example, contemplated constructing a 10,000-tonne-per-year solvent-separation plant for rare earth metals in the U.S. in 2012, with a preliminary CAPEX of $302 million[4]. Avalon canceled the plan two years later, citing prohibitive expenditures and plans to utilize existing processing capacity in France[5]. Plant construction and material costs are anticipated to have increased since 2012, exacerbating the cost and CAPEX constraints of processing key metals domestically. Therefore, it is necessary to develop novel, innovative, and alternative technologies that could exploit alternative sources of critical minerals.

[3] https://rmi.org/wp-content/uploads/2019/12/Low-Carbon_Metals_for_a_Low-Carbon_World.pdf
[4] Andrew Topf, "Processing plant to cost $302 million- 1/3 of Avalon's rare earth project capex," *Mining.com*, 2012.
[5] Timothy Boone, "Avalon Rare Metals not building Geismar plant," *The Advocate*, 2014.

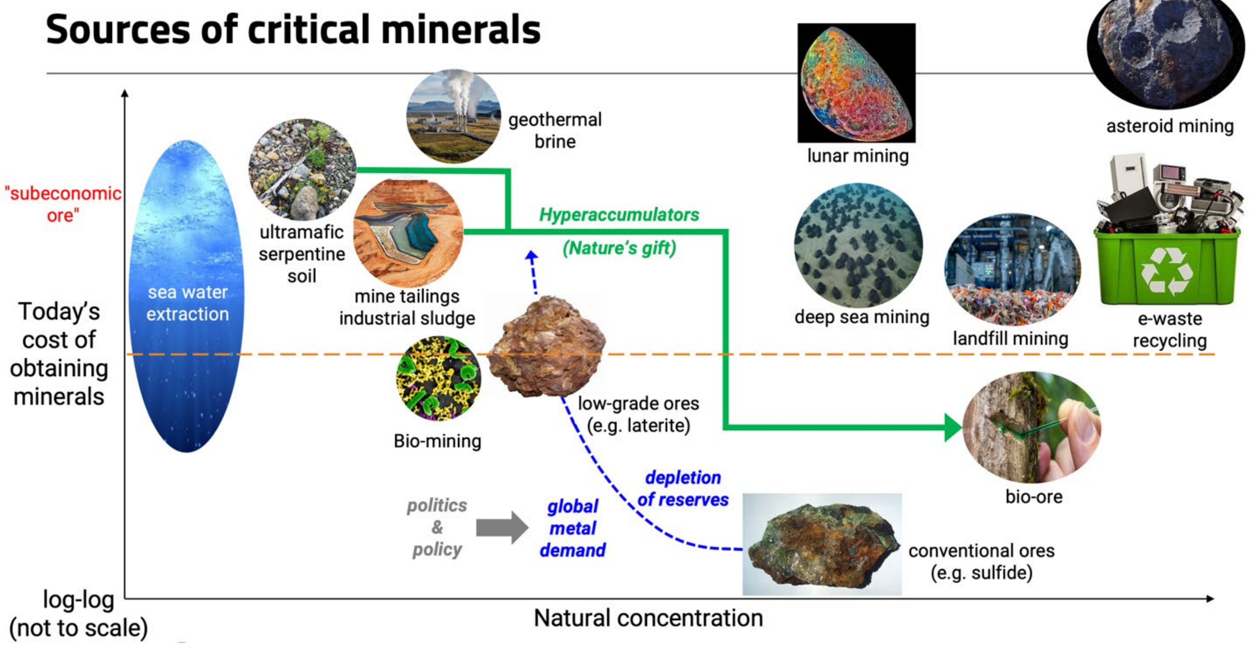

Figure 2. Comparison of various sources of critical minerals based on their natural concentrations and relative cost to obtain them from each source type (illustrative).

A recent investigation into alternative sources of critical minerals (Figure 2) was prompted by both the degradation of ore grades over time and the rising demand for secure critical mineral supply chains. There have been a number of potential solutions proposed, however, some of these methods are rather conceptual and impractical (asteroid mining, lunar mining), and the clean energy transition is happening so fast that recycling alone is unlikely to satisfy the increase in critical mineral demand in the short term[6]. Trace amounts of critical minerals such as nickel, cobalt, and rare earth elements exist in ocean water, but their dilute nature makes it challenging to discover the materials and concentrate it cost-effectively. Furthermore, it is unclear if the total amount of economically-accessible resources in U.S. ocean waters is sufficient to meet expected demand by the clean energy sector in 2050. These minerals/metals are also found dispersed in U.S. soils and surface rock, and it is estimated that there will be more than enough of this resource to meet the demand for a number of these minerals, including cobalt (Figure 3). Hyperaccumulator plants can preferentially extract certain minerals from the soil, naturally concentrating the mineral of interest. Phytomining, or cultivating these plants and collecting the concentrated version of the minerals/metals within them, could provide a way to supply the United States with domestically produced critical minerals/metals for the clean energy industry.

Phytomining

Phytomining entails the accumulation of specific metals in plants by root absorption and storage in plant cells, followed by the harvesting and processing of these plants (for example, burning) to produce bio-ore from which metals can be recovered. Tailored agricultural engineering could augment natural metal hyperaccumulation in plants, allowing metals to be extracted from terrestrial environments without the requirement for blasting, comminution, or a flotation stage, as in traditional ore mining. In the present state of the art for phytomining, traditional agronomy practices are used to boost rates of metal accumulation into biomass, and burning and smelting are used for post-harvest processing, which is

[6] "The Role of Critical Minerals in Clean Energy Transitions," International Energy Agency (IEA). 2021.

currently done in the laboratory and in hectare-scale demonstrations. Phytomining could potentially become a carbon-negative supply of critical minerals for the clean energy transition if optimized plants could be coupled with advancements in post-harvest processing, such as extraction without burning the biomass.

Phytomining could fill a key technology gap in the field of alternative metal sources. Phytomining 1) does not require the blasting, crushing, and other processes that microbe-based biomining requires; 2) has the potential to unlock terrestrial resources that are 10-200 times larger and 5 to 6 orders of magnitude more concentrated than those found in the U.S. exclusive economic zone ocean waters; and 3) takes advantage of the fact that plants naturally and efficiently break down rock, accumulating soluble metals that can be upgraded to cathode materials and other high-value chemicals at a lower cost. If phytomining is successful, it has the potential to unlock a significant reservoir of critical minerals in the top surface of the continental crust (Figure 3), potentially realizing a carbon-negative source of critical minerals in the United States.

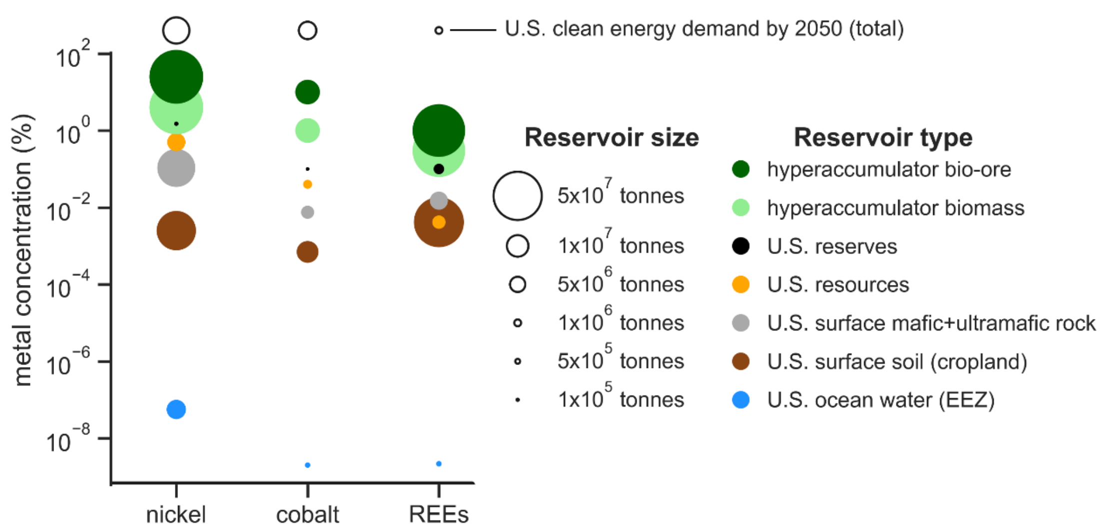

Figure 3: Hyperaccumulator biomass (light green circles) and bio-ore (dark green circles) are highly concentrated metal sources that have the potential to exceed the U.S. metal demand by “unlocking” the previously inaccessible and "subeconomic-to-mine" metals in soil (brown circles) and surface rock (grey circles). The U.S. resources (orange circles) represent all metal ores (concentrated metal deposits) that have the potential to become "economically mineable" with increased demand/price, while the U.S. reserves (black circles) represent those resources that are currently "economically mineable," due to concentration and other factors. The total amount of dissolved metals in the U.S. coastal ocean known as the Exclusive Economic Zone (EEZ) is shown (blue circles) – this estimate assumes 100% recovery of all metals in the EEZ, not including mixing. If metals can be extracted continuously year-to-year as EEZ water exchanges with the open ocean, this estimate will be higher. The estimated demand from electric vehicles (nickel, cobalt) and offshore wind (REEs) is shown in the open black circle above the axis for each metal, demonstrating that current, economic U.S. reserves are insufficient to meet all expected demand in the case of nickel and cobalt, and that alternative sources would be necessary for a fully U.S.-based metals supply chain. For REEs, the total supply of all REEs is shown. Data from USGS National Minerals Information Center 2021 Statistics and Information for Nickel, Cobalt, and Rare Earths.

Demand estimates include projections from the Princeton University Net-Zero America project.

Hyperaccumulators and Hyperaccumulation pathways in Phytomining

Plants that hyperaccumulate metals evolved in metal-rich soils and have a higher tolerance for metal content than other organisms. A number of these natural hyperaccumulator species are known, including *Odontarrhena chalcidica* (perviously *Alyssum murale*), *Phyllanthus rufuschaneyi*, *Phyllanthus balgooyi*, and *Pycnandra acuminata*[7]. Hyperaccumulators have predominately been used for phytoremediation, which is the removal of toxic metals from soil. Phytoremediation is used to remove low-value harmful metals from the environment, and the resulting biomass must be disposed of as hazardous waste. Phytomining, on the other hand, focuses on the harvesting and upgrading of high-value metals into industrially useful compounds before being sold. Nickel, cobalt, and rare earth elements are examples of metals that are naturally accumulated by plants and have high economic worth[8]. In lab and hectare-scale trials, some of these metal targets have been pursued. ARPA-E is seeking information on any metal target that is relevant to the clean energy transition and could be directly extracted non-destructively from non-ores (e.g. soils, surface rock, tailings, etc.) in terrestrial environments.

Environmental Considerations in Phytomining

Phytomining has the potential to be a carbon-negative, low-energy, non-destructive, and low-CAPEX source of critical minerals. Non-ore terrestrial resources, which are deemed subeconomic ores in conventional mining, could be "unlocked" through phytomining. ARPA-E is interested in potential transformative technological improvements in the field of phytomining that could secure entirely U.S.-based critical mineral supply chains. ARPA-E is also interested in learning more about potential environmental implications, such as the relative consequences of conventional mining and phytomining on GHG emissions, water consumption, land use, and other factors.

Current phytomining techniques

Nickel phytomining has been demonstrated in lab- and hectare-scale experiments[9]. Broadly, these techniques include harvesting crops grown on metal-rich mafic and ultramafic soils, burning the biomass to ash in the field, then acid-based extraction of the metal for purification and upgrading. ARPA-E is interested in any potential solution for extraction of critical minerals, particularly any technique that would result in a carbon-negative source of critical minerals in the United States, including both extraction and processing into upgraded metals suitable for battery and other clean energy supply chains. ARPA-E is interested in learning more about the obstacles to direct mineral extraction from terrestrial environments, as well as what technological breakthroughs would be required to develop a cost-effective and carbon-negative method for unlocking terrestrial mineral resources that does not require blasting, grinding, or a flotation step.

Please carefully review the REQUEST FOR INFORMATION GUIDELINES below. Please note, in particular,

[7] *Agromining: Farming for Metals* 2nd edition, 2021. Eds. Antony van der Ent, Alan J.M. Baker, Guillaume Echevarria, Marie-Odile Simonnot, Jean Louis Morel.
[8] Amelia Corzo Remigio, *et al.*, “Phytoextraction of high value elements and contaminants from mining and mineral wastes: opportunities and limitations,” *Plant Soil*, 2020.
[9] Philip Nti Nkrumah, *et al*., “The first tropical ‘metal farm’: Some perspectives from field and pot experiments,” *Journal of Geochemical Exploration*, 2019.

that the information you provide will be used by ARPA-E solely for program planning, without attribution. **THIS IS A REQUEST FOR INFORMATION ONLY. THIS NOTICE DOES NOT CONSTITUTE A FUNDING OPPORTUNITY ANNOUNCEMENT (FOA). NO FOA EXISTS AT THIS TIME.**

Purpose and Need for Information

The purpose of this RFI is solely to solicit input for ARPA-E consideration to inform the possible formulation of future research programs. ARPA-E will not provide funding or compensation for any information submitted in response to this RFI, and ARPA-E may use information submitted to this RFI without any attribution to the source. This RFI provides the broad research community with an opportunity to contribute views and opinions.

REQUEST FOR INFORMATION GUIDELINES

No material submitted for review will be returned and there will be no formal or informal debriefing concerning the review of any submitted material. ARPA-E may contact respondents to request clarification or seek additional information relevant to this RFI. All responses provided will be considered, but ARPA-E will not respond to individual submissions or publish publicly a compendium of responses. **Respondents shall not include any information in the response to this RFI that could be considered proprietary or confidential**.

Responses to this RFI should be submitted in PDF format to the email address **ARPA-E-RFI@hq.doe.gov** by **5:00 PM Eastern Time on May 26, 2022.** Emails should conform to the following guidelines:

- Please insert "Response to <insert RFI name> - <your organization name>" in the subject line of your email.
- In the body of your email, include your name, title, organization, type of organization (e.g. university, non-governmental organization, small business, large business, federally funded research and development center (FFRDC), government-owned/government-operated (GOGO), etc.), email address, telephone number, and area of expertise.
- Responses to this RFI are limited to no more than 12 pages in length (12-point font size).
- Responders are strongly encouraged to include preliminary results, data, and figures that describe their potential processes.

Questions

ARPA-E is interested in surveying stakeholders interested in phytomining in the U.S. within the scope of the approaches outlined above. The questions posed in this section are classified into several different groups as appropriate. Please provide responses and information about any of the following. ARPA-E does not expect any one respondent to answer all, or even many, of these prompts. Simply indicate the group and question number in your response. Citations are encouraged as appropriate. Respondents are also welcome to address other relevant avenues/technologies that are not outlined below.

General

1. How does phytomining compare with other alternative sources of critical minerals (e.g. extracting metals from seawater or algae, seabed nodules and deep sea mining, geothermal brines, e-waste recycling, landfill mining, lunar mining, asteroid mining, etc.) in terms of total

metal availability, feasibility of extraction and processing, scalability, potential cost, etc.? What are the advantages and disadvantages of these potential alternative sources compared to conventional mining?

2. What potential investments in conventional mining might allow for U.S.-based extraction and processing of critical minerals for fully U.S.-based supply chains, and would they be more valuable than investments in alternative sources of critical minerals?
3. What technical hurdles must be overcome for phytomining to progress from a lab-scale, academic demonstration phase to a successful and scalable private-sector-funded operation in the United States? What would be the anticipated time frame for such a transition?
4. What are the non-technical obstacles in phytomining that ARPA-E should be aware of (regulatory/policy impediments, environmental impact, etc.)?
5. Are there any commonalities between phytoremediation and phytomining that could be leveraged when considering larger-scale phytomining? Where, for example, has phytoremediation shown to be the most profitable? What are the most significant obstacles for phytoremediation startups and other businesses? What are the similarities and differences between these difficulties and those linked with phytomining?
6. What would be the next frontier in phytomining? What is the next "transformational" technology that would be meaningful to the clean energy transition?
7. Should phytomining be focused solely on the relative cost benefit of metal extraction, or should the value of carbon sequestration be considered as well?
8. What are some alternative cost-effective, scalable, and low-emission technologies that could compete with phytomining for extracting important minerals from non-arable soil?
9. Is it necessary for phytomining in the U.S. to rely solely on non-arable land in order to be cost-effective and scaleable? Should the use of arable land be in the scope? Consider potential challenges in ease of cultivation, harvesting, competition with food and energy crops, etc.

Mineral demand

10. What critical minerals would be best suited for phytomining in the United States, and why? What are the total annual yields (in kilograms of metal/kilograms of biomass and kilograms of metal/hectare) that phytomining can produce? Please provide the key assumptions and rationales.
11. What specific chemical forms of metals should be considered for phytomining (e.g. acceptable forms of metal for battery manufacturers)? Please list the metal, its chemical speciation and purity, as well as the end-user application. Are there any specific mineral forms that could be created more directly through phytomining and subsequent processes, or alternative routes based on terrestrial biomass?
12. What impurities are acceptable (metal impurities, organic impurities, etc.) or problematic for the above-mentioned target applications? At what concentrations are these impurities acceptable? Are there any applications for phytomined metals that do not require thorough organic compound separation before entering the manufacturing process?
13. What are the economic and technical advantages and disadvantages of phytomining natural sources (low-grade ores/ultramafic soil) vs. anthropogenic sources (mine tailings, wastes, contaminated soil)?

Hyperaccumulator strain and cultivation

14. What are the optimal species of plants (including shrubs, trees, or others) that could be domesticated in the United States for phytomining at scale when the following factors are considered? Please give as many examples as possible.

    a. soil conditions (including anthropogenic soil such as mine tailings)
    b. known metal accumulation pathways
    c. ease of cultivation (please give exemplary timelines from seeding to harvesting)
    d. ease of metal extraction
    e. other factors (please describe)
15. What are the potential barriers (climate, land characteristics, competing uses, etc.) to cultivating species described in the above question?
16. Can more than one type of hyperaccumulator species be co-cultured? Please provide detailed examples and rationales. What are the challenges associated with co-culturing hyperaccumulator species?
17. What is the rate of soil depletion using some of the best known hyperaccumulators (for example, hickory and fern species for REEs) if phytomining is employed continuously? Please provide the assumptions. What considerations (such as crop rotation) are required for continued accumulation? What factors should be taken into account (for example, root depth in the soil)? Is it conceivable for listed species to use rapid weathering, chelation, or other methods to "regenerate" accessible metals?
18. There had been incidents with unintentional seed dispersion, which resulted in the designation of some hyperaccumlator species as ‘noxious weeds’. What are the technical solutions to prevent such an event?
19. Should computational or data driven approaches (AI/ML) be considered for developing hyperaccumulator cultivars at the current stage of phytomining in the U.S.? Please describe specific examples.

Genetic Engineering of hyperaccumulators for optimal uptake and post-harvest processing

20. Are there known genetic pathways for uptake, transport, and accumulation of specific critical minerals? List the metal and any genes/pathways that have been characterized to date. Are there any emerging technologies for better understanding these pathways so they can be genetically manipulated?
21. Can genetic engineering or other techniques enable metal accumulation specifically in sap, or other forms, from which metals could be extracted economically?
22. What plant species could be optimally genetically engineered for extracting minerals and why? Please consider the following potential pathways for upregulation/optimization.
    a. root depth
    b. acid and chelator production
    c. resistance to high-metal environments
    d. ease of genetic transformation
    e. cultivation and harvesting
    f. terrains (typically steep and remote environment)
    g. other factors (please describe)
23. What could genetic engineering enable in terms of terrestrial extraction and low-CAPEX processing of critical minerals for clean energy buildout? What forms of metals can be hyperaccumulated in biomass? How can genetic engineering optimize the extraction and processing, in terms of where and how the metal is stored in the plant?
24. Should computational or data driven approaches (AI/ML) be considered for genetic engineering of the hyperaccumulators as well as surrounding microbes and microbiomes at the current stage of phytomining in the U.S.? Please describe specific examples.

Processing and Extraction

25. What existing processing capabilities and/or facilities in the United States could be used to extract critical metals from hyperaccumulator biomass and refine those metals for end uses, such as battery materials?
26. How could the accumulated metals be extracted from hyperaccumulators cost-effectively and with low carbon emissions? Please consider the following factors.
    a. Pre-treatment
    b. metal concentration
    c. conditions (temperature, pressure, pH, …)
    d. co-products (either another metal or other products)
    e. impurities
    f. biomass yield
    g. proximity to processing facilities
    h. processing costs
    i. other factors (please describe)
27. Are there any liquid-liquid separations that could be optimized to recover metals from biomass with or without burning the biomass? What factors limit cost and scalability of these separation methods, and are there any potential technological advancements that could help overcome these limitations?
28. What would be the profitable minimum scale of phytomining in the United States for a selected target metal, downstream processing route, and a target market?
29. What are the net CO_2 emissions of metallurgical processes that involve biomass burning followed by leaching vs. direct leaching?
30. What strategies could be employed to address the separation and purification issues that make critical element recovery economically challenging today? What is the primary challenge to overcome in these steps and why?

Environmental impact

31. What are the main environmental impacts of phytomining (global warming potential (GWP), acidification, eutrophication, etc.?)
32. Which environmental impacts of phytomining might be better than or worse than conventional mining?
33. How should environmental impacts of the main metal product and any byproducts be allocated?

Technology to Market

34. What might a potential large-scale U.S. phytomining value chain look like?
35. Can a potential phytomining business in the United States be small-to-medium sized (e.g. farmers) or does it require some level of vertical integration and scale? How would the business models vary?
36. What would be the profitable minimum scale of phytomining in the United States to consider generating co-product(s)? What are the desired co-product(s)? Is there any viable business model that can enable phytomining with the chosen co-product(s)?
37. What factors would drive the profitability of potential phytomining enterprises in the U.S. in the future?
38. Where in the U.S. could phytomining be best implemented?
39. Are there specific metals or first markets that U.S. phytomining should target?