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	Lithium occurrence and concentration grade around the nation
	Resources, extraction technologies, and economics
	November 2023
	Julian Chesnutt Nik Qafoku Rebecca Kreuzer
	U.S. DEPARTMENT OF Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory Richland, Washington 99354

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1.0 Introduction

1.1 General description of the project

Lithium, nickel, cobalt, manganese, and graphite are crucial to battery performance, longevity, and energy density. Rare earth elements are essential for permanent magnets in wind turbines and motors of electric vehicles. Electricity networks need a tremendous amount of copper and aluminum, with copper being a cornerstone for all electricity-related technologies. As such, the shift to a clean energy system is set to drive a massive increase in the requirements for these minerals.

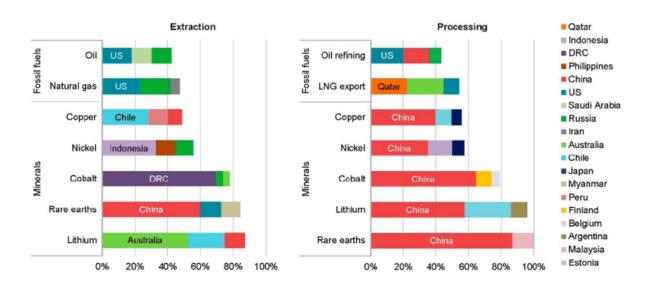


Figure 1. Share of the top three countries in extracting and processing selected minerals and fossil fuels (2019). Source: IEA (2021).

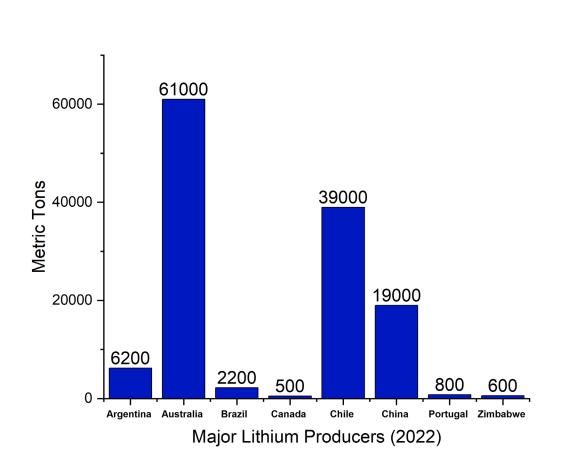


Figure 2. Major lithium producer **cou***ntries. Source: Institute for Energy Research, 2022 and Garside, 2023.*

A single country, China, currently monopolizes the global processing capacity of critical minerals (Fig. 1). However, Australia mines the most lithium ore (Fig. 2). Chili has ramped up lithium production recently and has exceeded China. Argentine production is primarily in Li carbonates and chlorides, Australia in spodumene, Brazil in Li concentrate, Canada in spodumene, Chile in Li carbonate, chlorides, and hydroxides, China in Li carbonate, Namibia in lepidolite, Portugal in lepidolite, Zimbabwe in petalite and lepidolite. US production numbers are withheld but are estimated at 5,000 metric tons per year (Fig. 2). part of the worldwide decarbonization efforts, the Biden Administration has been pushing to bolster the US lithium battery production capabilities. The goal is to reduce the country's reliance on foreign lithium supply and increase the nation's energy self-sufficiency. US lithium consumption has been relatively steady, around 2000-3000 metric tons annually (Fig. 3) for the last eight years. Still, it is expected to increase substantially as the electric vehicle and lithium battery needs increase.

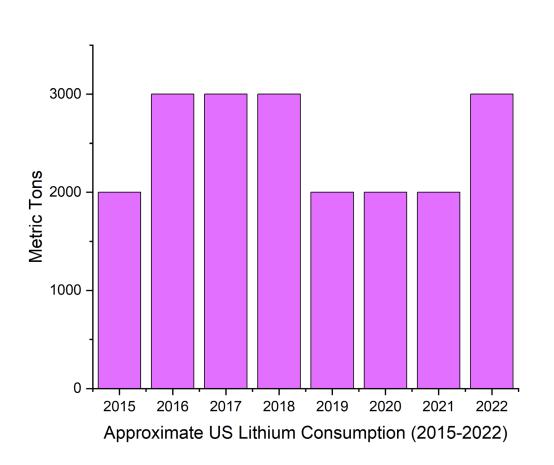


Figure 3. US lithium consumption (approximate), 2015-2022. Source: U.S. Geological Survey, Mineral Commodity Summaries, 2023.

The US has been importing \sim 20-50% more lithium than it's exported in the last eight years (Figs. 4 & 5), with the trade gap growing in the previous three years.

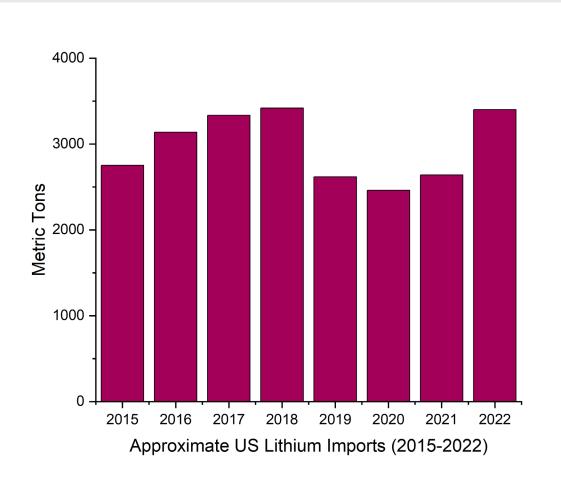


Figure 4. US lithium imports, 2015-2019. Source: U.S. Geological Survey, Mineral Commodity Summaries, 2023.

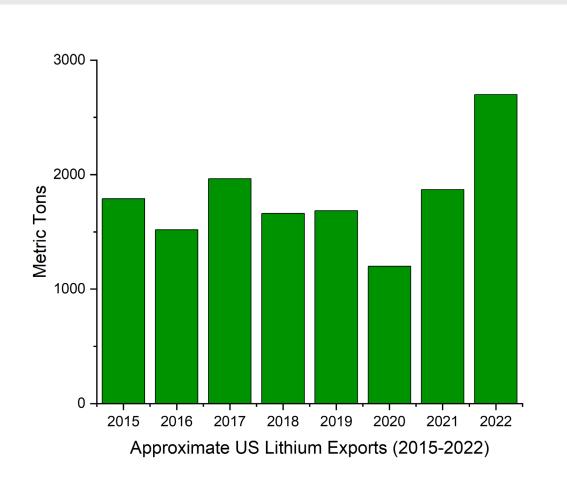


Figure 5. US lithium exports, 2015-2019. Source: U.S. Geological Survey, Mineral Commodity Summaries, January 2023.

The US must expand its domestic lithium manufacturing base to meet upcoming demands. The following sections of this report will cover many critical issues related to Li resources, supplies, processing, and extraction methods.

The global demand for lithium has skyrocketed in recent years, driven by the growth of the electric vehicle market and the transition to clean energy sources; this growth is the direct result of three international treaties—the Kyoto Protocol, Paris Agreement, and UN Sustainable Development Goals—all of which push for the integration of more renewable energy and clean storage technologies in the transportation and electric power sectors to curb CO₂ emissions and limit the adverse effects of CO₂-promoted climate change (Tabelin et al., 2021).

Lithium is a highly sought-after metal, and the demand for lithium minerals has increased considerably in recent years due to the crucial role of lithium compounds in lithium-ion battery technologies, which are widely employed in portable electronic devices, electric vehicles (EVs), hybrid electric vehicles (HEVs), and other power storage systems. As a result of this extremely high demand and the non-uniform distribution of economic lithium resources, lithium might encounter a potential supply crisis in the future.

Battery-grade lithium typically refers to lithium compounds or materials that meet strict specifications and quality standards. These standards ensure that the lithium used in batteries has a high purity level because impurities negatively affect battery performance and safety.

The primary lithium compounds used in battery-grade lithium are lithium carbonate (Li₂CO₃) and lithium hydroxide (LiOH). The purity of battery-grade lithium is typically specified in terms of impurity levels, including the concentrations of elements such as sodium, potassium, calcium, iron, and other metals. High-purity lithium is desirable because impurities can interfere with the electrochemical reactions within the battery and reduce its performance, cycle life/lifespan, and safety. Therefore, battery-grade lithium is carefully processed and purified to minimize impurities such as other metal ions, moisture, and organic contaminants.

The specific percentage of lithium considered battery grade can vary depending on industry standards and specific battery requirements. It's worth noting that different battery chemistries or applications may have slightly different purity requirements. Electric vehicles or energy storage systems demand higher purity to maximize performance and longevity, while other applications may have lower purity requirements. However, a standard benchmark for battery-grade lithium is at least 99.5% purity.

Overall, while 99.5% purity is a standard threshold for battery-grade lithium, it's essential to consider specific industry standards and individual battery manufacturers' requirements for precise purity specifications.

A typical run of mine ore can contain 1-2% Li_2O , while a typical spodumene concentrate suitable for lithium carbonate production contains 6-7% Li_2O (75% - 87% spodumene). Higher-grade concentrates with 7.6% Li_2O and low iron content are used in ceramics and more demanding industries. For more information, see <u>https://shorturl.at/frGSW</u>.

Over 60% of lithium produced in 2019 was utilized for the manufacture of lithium-ion batteries, the compact and high-density energy storage devices crucial for low-carbon emission electricbased vehicles (EVs) and secondary storage media for renewable energy sources like solar and wind (Tabelin et al., 2021). In 2019, the global market value of lithium reached around US \$213B and is forecasted to grow by around 20-25% until 2025 (Tabelin et al., 2021). The requirements for lithium (and other elements) in power generation, storage, and transport technologies were assessed until 2050 under six global energy scenarios (Junne et al., 2020). The results of this study showed that the material requirements increased with the degree of ambition of the scenarios, and the maximum annual primary material demand of the scenarios exceeded current extraction volumes by a factor of 12 to 143 for lithium. These authors recommended that future studies on the energy system transformation consider the influence of possible material bottlenecks on technology prices and substitution options.

Dessemond et al. (2019) give an overview of the lithium industry, including the lithium market, global resources, and processes of lithium compound production. It focuses on the production of lithium compounds from spodumene minerals.

1.2 Objectives

There is a need to document US lithium resources and current extractions and processing methods to determine what needs to be done in this area to secure lithium US independence. This (white) paper report focuses on answering the following questions:

- Where is the lithium supply?
- How do we get it out?
- How much will it cost?

Findings will be presented as a (white) paper report to the Advanced Materials and Manufacturing Technologies Office (AMMTO) and the Geothermal Technologies Office (GTO) to provide strategic support to the Offices and define future research opportunities.

This project also has the support of the AMMTO market sector manager, David Gotthold, and the Battery Materials and systems advisor, Mark Willey. Others supporting this project are Jie Xiao, a Battelle Fellow.

Regarding the EED strategic fit, this project will advance knowledge of energy decarbonization and support the Grid Storage Launchpad.

1.3 Approach and Deliverables

The following approach was used:

- 1. Data collection
 - a. Review the USGS databases.
 - b. Collect data on occurrence, concentration grade, types (e.g., oxides, carbonates, clay-bound, etc.), and extraction ability of the lithium minerals/rocks.
- 2. Mapping and classification of lithium resources
 - a. Make map(s) of lithium mineral resource's location, concentration grade, and types.
 - b. Build time series graphs of imported, exported, and consumed Li
- 3. Connect lithium occurrences with the appropriate (PNNL) extraction technology
 - a. Relate that to the appropriate extraction technology(ies)
 - b. Ideas (on what could be fundable work) to get the many low lithium concentration sources to yield battery-grade lithium.
 - c. Identify gaps to build a roadmap to lithium independence.
 - d. Ideas on utilizing the many low-grade lithium ores/sources to get them to battery grades; aka provide AMMTO ideas on what technologies/research to fund to transform US low-grade lithium resources into higher (battery-grade capable) sources, thus to lithium independence.
- 4. Economic evaluation by area
 - a. Do a first-pass economic feasibility assessment per area and types
- 5. Propose a way forward and future efforts.

The following deliverables will be part of this effort:

- 1. A white paper/PNNL letter report will be written and shared with the AMMTO and GTO market sector managers and program officers.
- 2. A brief communication article will be submitted for publication if funds are available next fiscal year.

2.0 Literature Review and Discussion

2.1 Lithium resources, minerals/rocks

Lithium is emerging as a pivotal chemical element for shaping the future, offering a solution to reduce our dependence on fossil fuels while catering to the growing demand for ecofriendly energy production. Although lithium remains a rarity in the cosmos, the formation of continental crust has facilitated the concentration of this essential element in exploitable deposits (Grew, 2020). New lithium resources have been consistently discovered and unearthed through unwavering exploration efforts, with estimations now reaching a staggering 89 million tons globally (DOE EERE, 2022). The mineral realm boasts a diverse array of 124 recognized lithium-bearing species (Grew, 2020), sparking vital research efforts. An illustrative instance of such research involves revisiting and enhancing the thermodynamic database for several lithium minerals, such as bikitaite, cookeite, elbaite, ephesite, hectorite, lepidolite, Li-mica, petalite, polylithionite, taeniolite, and zinnwaldite, a recent undertaking by Boschetti (2022).

According to the U.S. Geological Survey, there are approximately 20 sites in the United States that contain enrichments of lithium (Li) (<u>https://www.usgs.gov/data/lithium-deposits-united-states</u>) (Fig. 4). An essential property these sites share is their possession of a contained resource and historical lithium metal production exceeding 15,000 metric tons (Utility Dive, 2022). In the United States, the identified lithium resources stem from diverse sources, including continental brines, pegmatites, geothermal brines, hectorite, oilfield brines, and searlesite, amounting to an impressive 9.1 million tons (DOE EERE, 2022).

In 2018, lithium production within the U.S. was restricted to a single lithium-brine mining operation in Nevada. During that period, the U.S. had a considerable net import reliance, accounting for over 50 percent of its apparent consumption of lithium. Given the limited lithium production within its borders, the U.S. primarily relied on imports to meet consumer demands. Notably, the primary sources of these imports were Chile and Argentina (Utility Dive, 2022), emphasizing the significant role these countries played in meeting the nation's lithium requirements.

The following section of this report will delve into an assessment of the genesis of lithium deposits, encompassing their geologic formation. This will include an analysis of the varied types of rocks and minerals that compose these deposits, their prevalence, and the techniques utilized to characterize them, specifically those currently used to quantify lithium concentrations and amounts. To ensure a comprehensive analysis, the examination of data extended beyond the confines of the USGS database, incorporating supplementary insights drawn from a literature review of recent journal articles. The search phase was facilitated by employing Web of Science to search the literature, focusing on pertinent papers published within the last few decades. This endeavor encompassed the review of approximately 80 scholarly articles, most aptly referenced and cited within this document.

2.2 Genesis, types, and description of lithium rocks/minerals

Various research papers have encapsulated insight into the origins and formation of lithium deposits. A notable example is the work conducted, which sheds light on the crystallization process of miarolitic pegmatites. These pegmatites, characterized by their high-water concentration at relatively low pressures (1-3 kbar) and peralkaline melts, were studied in the context of the Konigshain region in Germany. This study underscores that the miarolitic pegmatites in Konigshain exemplify a diverse range of pegmatite types, with the processes occurring at this site representing those found in a majority of granitic pegmatites.

A distinct case emerges in China, where the most extensive lithium pegmatite ore occurrences are situated within the Songpan-Ganze orogenic hinterlands in East Tibet (Xu et al., 2020). Here, lithium pegmatites find their home amidst Upper Triassic turbiditic metasedimentary rocks. These formations are intricately tied to granitic intrusions, currently observable as gneiss domes, as delineated by Xu et al. (2020). This remarkable scenario highlights the geological interplay between granitic intrusions, metasedimentary rocks, and this region's resulting lithium-rich pegmatite deposits.

The earliest instances of lithium minerals with geological significance are traced back to lithium-cesium-tantalum (LCT) pegmatites, which emerged around 3,000 to 3,100 million years ago (Ma). This temporal dimension is particularly pivotal as it aligns with a crucial juncture in the development of the continental crust, marking a period of significant crustal evolution and its generation (Grew, 2020). Notably, this era is a pivotal landmark in Earth's geological timeline.

The insights of Grew (2020) further extend to the intriguing possibility of a connection between the advent of LCT-family pegmatites and the inception of plate tectonics. According to Grew's perspective, this correlation gains credence through the notable association between the prevalence of LCT-family pegmatites and the assembly of supercontinents (Grew, 2020). This implies a more profound interplay between the geological evolution of our planet and the emergence of specific mineral formations, adding layers of complexity to our understanding of Earth's dynamic history.

Lithium carbonate and hydroxide are predominant among lithium-based commercial products (as illustrated in Figure 6).

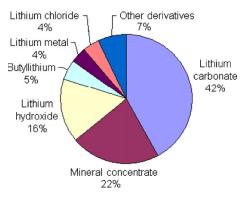


Figure 6. (Fig. 4 of Grosjean et al., 2012). Market shares of lithium-based commercial products. Based on data from Roskill [17].

Significant lithium resources are distributed across various geological settings, encompassing lithium-rich brines, pegmatites, and clay deposits. Each of these sources will be explored in greater depth below.

<u>Lithium-rich brine</u> deposits stand as the prevailing and widespread origin of lithium production. The extraction process becomes more intricate with the varying forms of lithium salts, such as lithium carbonate, chloride, and hydroxide. While lower lithium concentrations can be relatively straightforwardly refined to attain battery-grade quality, the refinement process may become more complex in higher concentrations. Each geological setting presents unique challenges and opportunities in extracting and refining lithium resources, reflecting the intricate interplay between geology, chemistry, and industrial processes in the quest for this essential element.

<u>Pegmatites</u> represent igneous rock formations renowned for harboring notable concentrations of lithium-bearing minerals, including prominent examples like spodumene, petalite, and lepidolite. The escalating global concern over alternative energy sources has propelled an increased demand for lithium, consequently driving heightened exploration efforts for lithium pegmatite deposits. Primarily sought after for their lithium content, these rock deposits are subjected to lithium extraction, typically involving mining, crushing, and chemical processing to extract the lithium content. Presently, spodumene sourced from pegmatite deposits is the primary contributor of lithium from ores. Nonetheless, future lithium sources are anticipated to encompass an array of other minerals, notably lepidolite, petalite, zinnwaldite, jadarite, and hectorite (Tadesse et al., 2019).

Among these, spodumene is a crucial source and holds a pivotal role, characterized by its exceptional lithium content and the efficiency of its extraction process. This mineral's significance is underscored by its substantial contribution to meeting the surging demand for lithium in the current energy landscape (Dessemond et al., 2019). The intricate interplay between these diverse minerals within pegmatite formations highlights their collective importance in pursuing a sustainable lithium supply.

Although comprehensive documentation of the geology concerning many of these deposits is conspicuously lacking in contemporary literature, it becomes apparent that pegmatites, as economic lithium sources, predominantly feature spodumene rather than other lithium-bearing minerals (Groves et al., 2022). These economically significant pegmatites, largely of Archean origin and distributed worldwide, commonly exhibit sub-horizontal to gently dipping configurations, distinct from the often near-vertical arrangement of pegmatite swarms. Additionally, they showcase intricate 3D geometries, marked mineralogical and geochemical zoning, and are ensconced within amphibolite-facies wall rocks (Groves et al., 2022).

According to Groves et al. (2022), the complex geometries and flat dips are consistent with syn-metamorphic emplacement in dilation zones within a compressional to transpressional regime. This context would have facilitated the injection of multiple successive pulses of lithiumenriched molten material and allowed for a more significant time for vertical pegmatite differentiation of volatile-rich pegmatitic melts during prolonged cooling and for spodumene to crystallize as the most common medium-to-high pressure/temperature phase within flat-lying lithium-rich zones (Groves et al., 2022). Again, this interpretation by Groves and colleagues underscores the complexity of the geological processes shaping these deposits and highlights the significance of geological and tectonic dynamics in influencing the formation and characteristics of these economically crucial pegmatites. Groves et al. (2022) provided insights into the diverse occurrences of lithium minerals, encapsulating the multifaceted ways lithium minerals are distributed within the Earth's geological formations. According to these authors, lithium minerals exhibit a diverse range of occurrences, predominantly, but not exclusively, falling into four distinct categories (Grew, 2020):

- Lithium–Cesium–Tantalum (LCT) Granitic Pegmatites and Associated Metasomatic Rocks: One prominent occurrence of lithium minerals involves their presence within LCT granitic pegmatites, often accompanied by metasomatic rocks. This intricate geological context provides a conducive environment for forming these minerals.
- 2. **Highly Peralkaline Pegmatites:** Lithium minerals also find their place within highly peralkaline pegmatites. These specific types of pegmatites, characterized by their elevated peralkaline nature, contribute to the formation and concentration of lithium minerals.
- 3. **Metasomatic Rocks Not Directly Associated with Pegmatites:** Beyond pegmatites, lithium minerals can be identified in metasomatic rocks that are not directly affiliated with pegmatite formations. This distinct geological setting offers an alternative avenue for the presence of these minerals.
- 4. **Manganese Deposits:** Additionally, lithium minerals can manifest within manganese deposits. This unique occurrence highlights the interconnectedness of various geological processes in contributing to the presence of lithium-rich minerals.

<u>Lithium clays</u>, exemplified by minerals like hectorite and micaceous lithium-bearing ores, hold promise as an additional viable lithium source, complementing pegmatites and lithium-rich brines. Nevertheless, a consensus exists among certain researchers that a comprehensive understanding of how lithium and its associated minerals are distributed within certain ore bodies remains limited (Aylmore et al., 2018a).

In a study led by Aylmore et al. (2018a), the investigation of micas revealed distinct polymorphs exhibiting variations in chemical compositions, including parameters such as the aluminum-to-silicon ratio, fluorine content, and sodium levels, alongside differing lithium grades. Notably, the bulk of the lithium content (approximately 1.2-1.5% Li) was found to be associated with lepidolite or zinnwaldite minerals, both of which comprise lithium muscovite, trilithionite, and polylithionite grains (Aylmore et al., 2018a). The form and structure of lithium-bearing micas exhibited variability across different deposits, with only minor quantities (similar to 1%) of other lithium-bearing minerals, like spodumene, elbaite, and beryl, present within these samples.

In the context of lithium clays, a clay formation containing lithium from China's Guizhou Province includes minerals such as illite, chlorite, kaolinite, pyrite, and anatase (Zuo et al., 2022). Further investigations have explored exomorphic halos, mineral-altered zones forming around pegmatite bodies and rich in elements like Li, Rb, Be, B, Cs, Sn, and Ta. These halos, with thicknesses of 2-6 meters, were identified in both mica schists and granitic rocks adjacent to spodumene pegmatites, specifically within the Leinster pegmatite belt in southeast Ireland) (Barros et al., 2022). These findings collectively underline the diversity and complexity of lithium distribution across various geological contexts and the continuous efforts to comprehend and tap into lithium resources more effectively.

Other lithium resources with a relatively lower lithium content are listed below.

<u>**Primary minerals**</u> like olivine, clinopyroxene, and orthopyroxenes also bear lithium, albeit in smaller quantities, as revealed by Kil (2010). This research indicated that olivines and

orthopyroxenes contain lithium in the range of 2.2 to 5.0 ppm and 2.1 to 6.4 ppm, respectively. In contrast, clinopyroxenes exhibit higher lithium concentrations, ranging from 2.0 to 8.4 ppm, indicating their tendency towards preferential lithium enrichment. In the realm of granitic pegmatites, alkali feldspar crystals have been noted to incorporate lithium in amounts spanning 9 to 350 ppm, as pointed out in the study by Maneta and Baker (2019). Notably, the study also underscored elevated lithium concentrations in quartz, ranging between 9 and 365 ppm. Muscovite crystals display the highest lithium concentrations, measuring between 562 and 6710 ppm.

Importantly, this study did not establish consistent trends in the distribution of lithium in quartz and muscovite concerning their proximity to spodumene or the originating zones. Compared with lithium-poor and potentially unproductive pegmatites in the Moblan region of Quebec, Canada, alkali feldspar, quartz, and muscovite they consistently exhibited higher lithium concentrations. This comparison highlights the distinct lithium enrichment in specific minerals within these geological contexts, emphasizing the intricate variability present in the distribution and composition of lithium-bearing minerals.

Geothermal brines. While commercial lithium production currently relies on conventional methods like saline salar brine extraction and spodumene ore processing, there is a growing interest in geothermal brines as an emerging source (Toba et al., 2021). The study by Toba et al. (2021) examined the feasibility of extracting lithium from geothermal brines in the United States. Through a comprehensive modeling analysis, the study evaluated both the potential for lithium extraction from geothermal brines and the potential implications on the supply chain. The results indicated that geothermal brines have the potential to contribute significantly, with estimates suggesting that lithium sourced from these brines could make up around 4% to 8% of the total lithium supply in the United States. Moreover, the study demonstrated that this source of lithium extraction could also be economically viable. This research underscores the shifting landscape within the lithium production industry, as alternative sources like geothermal brine are being explored to diversify the supply and meet the increasing demand for this vital resource.

Petroleum rock brines have emerged as a potential untapped source of lithium. A groundbreaking study led by Lee (2022) aimed to assess the production feasibility of lithium from this novel source and identify the factors influencing its viability. This study introduced a pioneering approach, offering insights into the potential production capabilities of lithium from petroleum rock brines. It conceptualized the key parameters pivotal in predicting lithium production potential from brines in diverse petroleum source rock systems and outlined the importance of quantitatively investigating these parameters. The results of this investigation hold the promise of bolstering and diversifying the lithium supply. By exploring the uncharted territory of lithium extraction from petroleum rock brines, this study contributes to the ever-evolving landscape of lithium sourcing. It potentially opens up new avenues for enhancing the availability of this crucial resource and augmenting the overall lithium supply chain.

Certainly, **soils** can also emerge as a valuable source of lithium. A recent study by Ng et al. (2023) demonstrated the potential of this novel lithium source. Employing a digital soil mapping framework, the study ingeniously merged data derived from contemporary geochemical surveys and various environmental factors influencing soil formation. This integration facilitated the prediction and mapping of aqua-regia-extractable lithium content across the vast expanse of Australia, covering an area of 7.6 million square kilometers. The outcomes of this study unveiled predictive maps showcasing elevated lithium concentrations. These hotspots of lithium concentration were notably clustered around existing mining

operations and other regions that exhibit the potential for anomalously high lithium content, albeit awaiting verification. Again, this pioneering research underscores the multifaceted ways lithium can be sourced from natural environments, and it provides an essential steppingstone for harnessing soil-derived lithium as a prospective contributor to the overall supply of this valuable resource.

Other unconventional lithium sources like <u>submarine/deep-sea ferromanganese (Fe-</u><u>Mn) nodules</u> and <u>crusts, industrial wastes</u> (e.g., desalination brines, geothermal brines and coal fly ashes), <u>mining wastes and effluents</u>, and <u>extra-terrestrial materials</u> were also explored in a recent publication (Tabelin et al., 2021).

Another noteworthy avenue for sourcing lithium resides in <u>recycled lithium batteries</u>. Recycling spent lithium-ion batteries offers a means of harnessing secondary resources to bolster lithium supplies (Meng et al., 2021). As detailed by these authors, recycling these batteries involves several stages, including disassembly and separation of cathode and anode materials, leaching of shredded components, and the subsequent retrieval and separation of metals. Meng and colleagues (2021) underscore the importance of tailoring recycling processes to cater to various applications' diverse compositions of batteries. The evolving landscape of battery technologies necessitates the development of a robust and sustainable recycling approach capable of efficiently recovering metals from a wide array of battery types. In their comprehensive review, the authors thoroughly examine existing lithium recovery methodologies, including those presently employed in industrial settings. This serves not only to inspire further technological advancements but also to guide the development of novel processes that align with the principles of sustainable lithium recovery. Recycling lithium batteries offers a promising strategy to extract additional value from discarded batteries and contribute to the overall lithium supply.

2.3 Occurrence

Lithium-bearing rocks and minerals, such as pegmatites and a series of other resources mentioned in previous sections of this report, need to be 5% > Li to be considered economically feasible to produce battery-grade lithium. As the demand for lithium continues its upward trajectory, exploration efforts are steadfastly underway to uncover and exploit fresh lithium resources across the globe. It's crucial to recognize that lithium reserves aren't uniformly spread worldwide, leading to substantial variations in the concentration and accessibility of lithium deposits.

In a conversation with Utility Dive, Venkat Srinivasan, who serves as the director of the Argonne Collaborative Center for Energy Storage Science at Argonne National Laboratory and deputy director of the Joint Center for Energy Storage Research, she posed a pivotal query: "Where is the supply?" (Utility Drive, 2022). This inquiry underscores the paramount importance of understanding the geographical and geological distribution, depth, accessibility, and quantities of lithium resources.

It's imperative to emphasize that the potential resources encompassing lithium-bearing rocks and minerals, like pegmatites, alongside other sources detailed in previous sections, must contain lithium concentrations exceeding 5% to be deemed economically viable for producing battery-grade lithium. This underscores the importance of this parameter when evaluating potential lithium resources to ensure their practical and sustainable contribution to the growing global lithium demand.

<u>World resources.</u> The global distribution of lithium resources showcases a diverse array of deposits and sources. Lithium-rich brines are a prominent resource, often found in arid regions where lithium-enriched groundwater accumulates over geological time. A central hub for these brines is the "Lithium Triangle," spanning parts of Argentina, Bolivia, and Chile. The Salar de Atacama discovery in Northern Chile in 1969 marked the initiation of identifying a significant continental region for lithium brines, with the Central Andes now contributing substantially to the world's lithium production (Cabello, 2021). Chile is a significant producer, driven by the impressive size of the Salar de Atacama and the high-quality lithium brines it yields, responsible for a notable 23% of global lithium production in 2019 (Cabello, 2021). Lithium brine production, reserves, resources, and exploration were covered in detail in the review paper by Cabello (2021).

China and the United States also boast substantial brine deposits, such as the Clayton Valley in Nevada. Australia and Canada, on the other hand, emerged as significant producers of pegmatite lithium sources. Additional noteworthy sources include lithium clay deposits in various countries, including Li-bearing clay from China's Guizhou Province, comprising illite, chlorite, kaolinite, pyrite, and anatase (Zuo et al., 2022).

Other resources include the spinel lherzolite xenoliths found in Boeun, Korea, that have protogranular to porphyroclastic textures and are enclosed in a Miocene alkali basalt (Kil, 2010) and the Leinster pegmatite belt in southeast Ireland which comprises several largely concealed Li-Cs-Ta albite-spodumene-type pegmatites (Barros et al., 2022). Even the largest pegmatite deposits, such as those at Greenbushes (Australia) and Manono Kitolo (Democratic Republic of Congo), have estimated resources that are similar to only an average brine deposit (Kesler et al., 2012). For this reason, continuous, long-term production from pegmatites will require extensive exploration and discovery of new pegmatite deposits and districts.

The Jiajika and Markam lithium pegmatites in China, the largest deposits in the Songpan-Ganze orogenic hinterlands, East Tibet, are pivotal lithium ore deposits. These pegmatites, hosted in Upper Triassic turbiditic metasedimentary rocks linked to granitic intrusions manifested as gneiss domes, contribute significantly to China's lithium resources (Xu et al., 2020).

Comparing lithium resources across different types of deposits, a study by Kesler et al. (2012) underscored the substantial variation in their scale. The average brine deposit, boasting a resource of 1.45 million metric tons (Mt) of lithium, exceeded the average pegmatite deposit (0.11 Mt Li) by over an order of magnitude. Notably, the vast Atacama (Chile) and Uyuni (Bolivia) brine deposits have a much larger total lithium resource of 21.6 Mt Li. The distinct advantage of brine deposits lies in their capacity for large-scale, long-term lithium production. However, the authors cautioned that individual brine deposits can significantly differ, and success in one does not guarantee the same in others. Despite their smaller size and total estimated resource (3.9 Mt), pegmatites remain pertinent due to their widespread distribution and reduced susceptibility to supply disruptions. Their more lithium-dominant compositions also facilitate flexibility in response to market shifts (Kesler et al., 2012).

Other intriguing sources, such as lithium-rich deposits through interactions with brines and hydrothermal solutions, including the Jadar (Serbia) and King Valley (USA) deposits, offer estimated resources of about 3.4 Mt Li. Unusual brines in oilfields and geothermal fields, like the Salton Sea geothermal field in the USA, carry an estimated 2 Mt Li. Although these sources necessitate novel processing methods, their lithium-rich compositions and substantial size render them essential contributors to the lithium supply (Kesler et al., 2012).

The lithium resources within these diverse deposits reported in the study by Kesler et al. (2012) amount to 31.1 Mt Li, surpassing the estimated lithium demand of up to 20 Mt Li (including recycling considerations) across all markets until 2100. However, these authors cautioned that these two estimates' differences should be seen mainly as a challenge rather than a comfort. Evaluation of the economic extractability of these resources will require significant investments and result in only partial success (Kesler et al., 2012). While the disparity poses a challenge, it also underscores the potential for continued exploration, investment, and advancements in extraction technologies, ensuring a sustainable lithium supply for the foreseeable future (Kesler et al., 2012).

A significant discovery was announced when this report was written (i.e., <u>on August 21</u>, <u>2023</u>) about a high-grade lithium mineralization at the Frazer Lake Mound Property in Northwestern Ontario, Canada. This is the first-ever lithium mineralization identified in Northwestern Ontario's Frazer Lake Mound Property. A high-grade zone with an average of 6.82% Li₂O, peaking at 7.26% Li₂O, was identified, underscoring high potential. About a 9-kilometer trend of enriched lithium-cesium-tantalum pegmatite veins and dykes was placed in this region.

United States Resources. A list of the lithium resources within the United States is provided below. Various exploration projects are ongoing in multiple states, aiming to assess and develop additional lithium resources from brines, pegmatites, and other sources (Fig. 3). Lithium in Kings Valley was discovered in the 1930s and has been mined since 1956 (Asher-Bolinder, 1991). The Bonnie Claire deposit is currently under exploration (Lane et al., 2018; Samari et al., 2021). Silver Peak is part of the Clayton Valley mineral district and has operated since 1966. Rhyolite Ridge is a new project undergoing exploration and development. Searles Lake has brine, evaporite, and sediment ore deposits and has been mined for borax since the late 1800s. Fort Cady is another new brine and ore project undergoing exploration and development. Source: Karl et al., 2019. The Wah Valley brine deposit is part of the Great Salt Lake deposit area. If more than one deposits is found in a given area, the average and standard deviation is provided. The resource-rich sites are in different states, such as Arkansas, California, Nevada, South Dakota, North Carolina, Montana, Maine, and Utah. It's also worth noting that several deposits, although excluded from the June 1, 2020, USGS database due to not meeting the lithium content threshold, are also present. These deposits can be found in states like Arizona, Colorado, the New England region, New Mexico, South Dakota, and Wyoming (Utility Dive, 2022).

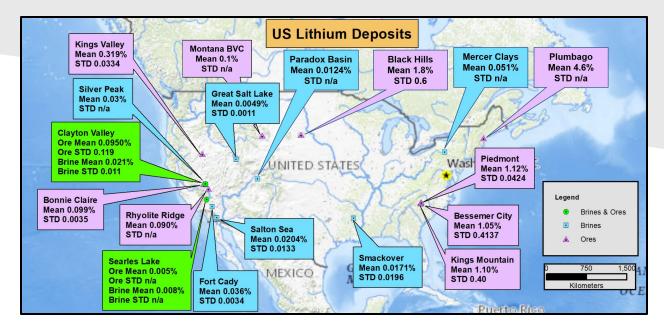


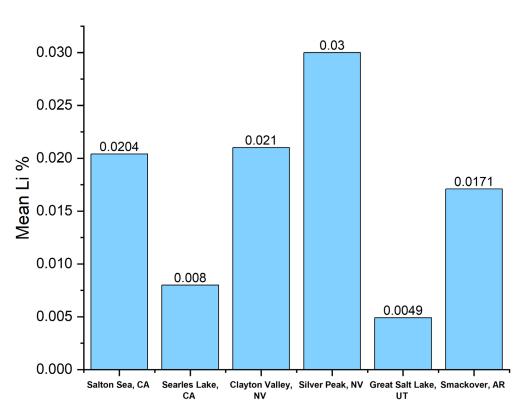
Figure 7. Location of lithium deposits in the US with average lithium content. Kings Valley contains the Thacker and McDermitt Caldera deposits.

2.3.1 Brines

- a. <u>Clayton Valley in Nevada</u> holds a prominent position within lithium resources. Renowned for its significant lithium deposits, the <u>Clayton Valley</u> is historically associated with brines' lithium production and stands out as the solitary lithium producer within the United States. This mine's lithium extraction legacy reflects Clayton Valley's significance in contributing to the country's lithium supply. Clayton Valley has three primary deposits, Zeus, Cypress, and a brine operation in the <u>sou</u>thern portion (Figs. 7 & 8).
- b. The region surrounding <u>the Salton Sea area in California</u> also possesses substantial lithium-rich brines with notably high lithium concentrations. This locale has garnered attention due to its potential as a source of lithium. Numerous projects are underway to investigate the feasibility of extracting lithium from these brines using methods that prioritize environmental sustainability. The focus on eco-friendly techniques underscores the commitment to responsible resource utilization while tapping into the valuable lithium resources in the Salton Sea area (Figs. 7 & 8).
- c. <u>Paradox Basin in Utah</u> stands out for its noteworthy lithium-rich brine deposits. These deposits originate as underground waters gradually extract lithium from rock formations, leading to its accumulation in concentrated brines. Spanning more than 4,000 acres, <u>this basin</u> harbors extensive claims focused on the exploration and, potentially, extraction of lithium. The particular emphasis here lies in brines connected with the potash bed horizons. It is known for its lithiumrich brine deposits, formed when underground waters leach lithium from rock formations and concentrate it in brines. It holds over 4,000 acres of claims in the Paradox Basin. It is well advanced with low-cost plans to explore for and potentially extract lithium from brines associated with the potash bed horizons. The Paradox Basin has made significant strides, having progressed well in

developing cost-effective strategies for the exploration and potential extraction of lithium from these brines. This concerted effort aligns with the growing recognition of lithium as a valuable resource and highlights the basin's promising potential to contribute to the expanding lithium supply (Figs. 7 & 8).

- d. The <u>Wah Wah Valley</u> region in Utah also boasts significant lithium brine resources, adding to the collective lithium reserves within the United States. Lithium brines in this region add to the diversity of lithium sources across the country and contribute to the overall portfolio of available lithium resources in the U.S. (Figs. 7 & 8).
- e. Last month's announcements indicate Arkansas (the town of Magnolia and surroundings) could become the U.S. lithium exploration and production epicenter—companies like Exxon Mobil plan to extract lithium from brine water to help power electric vehicles. An influx of workers and trucks could give the town of Magnolia and nearby counties an economic boost after years of decline. <u>The Smackover Formation</u> has North America's highest reported lithium in brine values. According to the Wall Street Journal, ExxonMobil plans to build extensive lithium processing facilities in the region, which could produce up to 15 percent of the global lithium output (Figs. 7 & 8).
- f. Efforts are underway to extract lithium from geothermal brines in the Salton Sea in California (DE-FOA-0002823, DOE EERE, 2022) (Figs. 7 & 8).



Brine & Evaporite Deposit Name, State

Figure 8 . Major US lithium brine deposit average concentration by percentage. Source: Karl et al., 2019.

2.3.2 Ores (Spodumene/Pegmatite)

- g. <u>King Mountain in North Carolina</u> carries historical significance as a site of lithium production linked to spodumene-bearing pegmatite deposits. While it has played a role in lithium extraction, production has remained relatively limited. Currently, it does not stand as a prominent source of lithium on a larger scale (Figs. 7 & 9).
- h. <u>The Piedmont region, spanning Georgia and South Carolina,</u> holds promise as a potential source of lithium. Within this area, lithium-bearing spodumene pegmatites are found. Recently, interest has been resurgent in exploring these resources to bolster domestic lithium production, indicating a growing recognition of the strategic value of utilizing local lithium sources (Figs. 7& 9).
- Black Hills region of South Dakota has historical significance for its spodumene (LiAlSi₂O₆) megacrystal deposits (see a recent communication in this link). The Black Hills hold significant lithium production potential and have been known for their spodumene-bearing pegmatite deposits, which contain valuable

lithium-bearing minerals. However, exploiting these resources involves complex geological, technological, and environmental considerations. Another critical factor is the economic viability of extraction, which depends on factors such as lithium prices, technological advancements, regulatory framework, and ecological sustainability. In summary, South Dakota, particularly the Black Hills region, is recognized for its lithium resources, contributing to the broader effort to secure diverse sources of this valuable element to support various technological and industrial applications (Figs. 7 & 9).

Recently, the mechanisms behind the formation of these crystals have been elucidated in a study conducted by Sirbescu and colleagues in 2023 (Sirbescu et al., 2023). An innovative two-step methodology for comprehensively characterizing the distribution of trace elements within sliced crystals was introduced. This technique entails two stages:

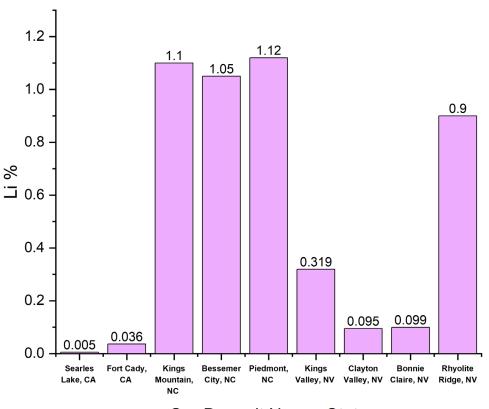
- Portable X-ray Fluorescence (pXRF): In this stage, data is collected across a square grid with a step size ranging from 0.5 to 1 centimeter. This allows for the initial assessment of the crystal's elemental distribution.
- ii. Benchtop Micro-X-ray Fluorescence (mu XRF): For a more detailed analysis, benchtop micro-X-ray Fluorescence is employed at a smaller step size, typically equal to or greater than 25 micrometers. This technique is applied to crystals or portions that have undergone prescreening using pXRF.

By combining these two techniques, the study facilitates an enhanced understanding of the trace element distribution within spodumene mega crystals of the <u>Black Hills region</u>, thereby shedding light on their formation mechanisms. This approach underscores the commitment to advancing scientific knowledge and refining analytical methodologies within the geological realm.

The Plumbago North deposit in Newry, Maine, has recently garnered attention j. due to the discovery of spodumene resources, focusing on the fascinating Plumbago North deposit. This newfound deposit has been the subject of a recently published paper by Sirbescu et al. (2023). Despite years of observation and speculation, the Plumbago North deposit presents intriguing puzzles that warrant further investigation. In their study, the authors propose that insights into the primary growth mechanisms of spodumene and optimization of lithium extraction can be gleaned from in-situ trace element geochemistry and zoning patterns within the mineral. A particularly notable method employed in this research is the integrated approach of portable X-ray Fluorescence (pXRF) and benchtop micro-X-ray Fluorescence (mu XRF), which proves valuable for characterizing composition and alterations in lithium ore. This integrated method enhances understanding chemical variations and zoning patterns within coarse to megacrystic minerals. It offers the potential for effective pre-screening of samples before employing other microanalytical techniques. The study underscores the potential of this innovative approach to advance knowledge about spodumene growth mechanisms, extraction optimization, and the broader understanding of chemical variations within minerals. This multidimensional

investigation holds promise for uncovering critical insights into the geological processes shaping mineral deposits like the Plumbago North deposit. Additionally, the integrated techniques open a new venue for investigating chemical heterogeneities and zoning patterns within coarse to megacrystic minerals. They may serve as an excellent sample pre-screening before other microanalytical techniques (Fig. 7)

k. Montana has emerged as a noteworthy location for lithium-bearing pegmatites across various regions. As mentioned in the previous sections of this report, these igneous rocks contain minerals like spodumene that are rich in lithium. Other formations, such as the lithium-rich beds, crop out in a band about 1.3 km long by 0.3 km wide near the head of Beaver Creek, about 14 km northwest of Lincoln, Montana. These beds consist of laminated marlstone, oil shale, carbonaceous shale, limestone, conglomerate, and tuff-some parts of this sequence average almost 0.1 percent lithium. However, the lithium-bearing rocks are too low in grade and volume to be economical. While the scale of lithium production in Montana has not reached the levels in some other regions, the state's lithium potential is gaining attention due to the increasing demand for lithium for battery production and other applications. The presence of these rocks underscores Montana's contribution to the growing landscape of lithium exploration and production, aligning with the broader global efforts to secure diverse and sustainable sources of this valuable resource. While Montana's lithium resources are part of the more comprehensive picture, their development will depend on various factors influencing the lithium market and extraction processes (Fig. 7)



Ore Deposit Name, State

Figure 9 . Major US lithium ore deposit average concentration by percentage. Source: Karl et al., 2019.

2.3.3 Other Resources

- Ideas exist to extract lithium from <u>oil and gas brines</u> and fly ash piles from coalfired power plants (Taggert et al., 2016).
- m. Clay mineral resources (Rozelle et al., 2021). The Mercer Clay bed in central Pennsylvania has produced feedstocks for the refractory industry in the USA and has also been investigated as a source of alumina and lithium. The work reported here includes reviewing the clay types and minerals involved, past mineral processing and extractive metallurgy test work, and new research results from a renewed investigation of the deposit as a polymetallic resource. This continued work has found lithium contents that exceed 1,000 ppm, lying directly below the overlying Mercer coal, where the alumina content ranged from 32 to 34 wt%. Total rare earth concentrations were somewhat lower than found elsewhere in the region, and the highest contents were also stratigraphically close to the coal. Further work is required to establish the mineral hosts for lithium and rare earths and to define the extent of enriched alumina, lithium, and rare earth concentrations (Fig. 7)
- n. The newly discovered <u>clay deposit on the border of Oregon and Nevada</u> (<u>McDermitt Caldera site</u>) was described by a team of volcanologists and

geologists from Lithium Americas Corporation, GNS Science, and <u>Oregon State</u> <u>University (Figure 10)</u>. The team provided evidence that this site may host some of Earth's largest known lithium deposits. In their project, reported in the journal <u>Science Advances</u>, Thomas Benson, Matthew Coble, and John Dilles studied parts of the caldera and developed a theory to explain how so much lithium was formed in the area. Li concentrations increase with decreasing clay (001) dspacing, demonstrating that the higher grades are associated with <u>the illite</u> <u>clays</u>. The illite-bearing claystone at McDermitt Caldera is a geologic feature located in the western United States, approximately 45 kilometers long and 35 kilometers wide. It is believed to have formed around 19 million years ago as part of the Yellowstone hotspot, a geological phenomenon responsible for creating a series of calderas.

In 2017, a team of researchers suggested that a specific area within the caldera known as Thacker Pass may hold one of the largest lithium sources ever discovered. Their theory proposes that the caldera's lithium deposits were formed through geological processes. Initially, a volcanic eruption occurred in the region, releasing various elements, including lithium, into the environment. Following the volcanic activity, hydrothermal enrichment took place. Magma from deep underground moved toward the caldera's center, creating the Montana Mountains. This movement led to faults, fissures, and Earth's crust fractures. The marks, cracks, and fractures created during the volcanic and tectonic activity allowed lithium to migrate toward the surface from deeper geological layers. This migration process contributed to the accumulation of lithium-rich deposits within the McDermitt Caldera. As lithium migrated, it interacted with minerals in the subsurface. This interaction transformed certain minerals, such as smectite, into illite. The illite deposits were concentrated along the southern rim of the caldera. Overall, the combination of volcanic activity, tectonic processes, and hydrothermal enrichment played a crucial role in the formation and concentration of lithium deposits within the McDermitt Caldera, particularly in the Thacker Pass area. This discovery has significant implications for lithium mining and the global supply of lithium, given the increasing demand for this element in various industries, including battery production for electric vehicles (Figs. 7 & 10).

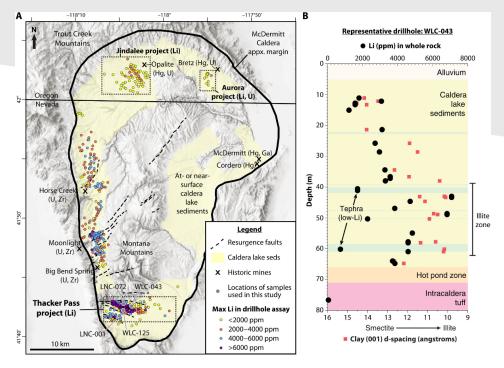


Figure 10. McDermitt Caldera lithium area. Source: Benson et al., 2023.

2.4 Mineral/rock characterization

Recent years have seen a growing body of research focusing on mineral characterization for lithium exploration. These studies explore the lithium-bearing mineral species' occurrence, distribution, and associated properties. Researchers have utilized different analytical techniques, including advanced spectroscopic and microscopic methods, to identify and quantify lithium-bearing minerals accurately. These efforts contribute to a comprehensive understanding of lithium-rich deposits and their potential for extraction.

Characterization studies are crucial in lithium exploration, extraction, and subsequent utilization for various energy-related applications. Two key aspects stand out in these studies: the identification of lithium-bearing minerals and accurately determining lithium concentration and grade within mineral samples or assemblages. These aspects are paramount due to their direct influence on lithium extraction processes and subsequent applications.

The first aspect, the identification of lithium-bearing minerals, is pivotal as different minerals possess distinct physical and chemical properties that significantly impact the efficiency and effectiveness of lithium extraction methods. Accurately identifying these minerals helps to tailor extraction processes to specific mineral types, optimizing resource utilization and enhancing overall operational efficiency.

The second aspect, determining lithium concentration and grade precisely, is equally crucial. This involves quantifying the amount of lithium present in mineral samples or rock formations, allowing for the assessment of resource potential and the feasibility of extraction efforts. Accurate measurement of lithium content aids in making informed decisions regarding

the economic viability of mining operations and helps in estimating the potential yield of lithium for energy applications.

Various analytical, microscopic, and spectroscopic techniques are employed to extensively characterize rocks, minerals, and brines, aiming to ascertain the presence of lithiumbearing materials and their lithium content. The identification and quantification of lithium involve a range of methods. Noteworthy research efforts have encompassed in-depth characterization studies of pegmatites, pegmatite-associated granitic systems, and rare-metal pegmatites (Beskin and Marin, 2018, 2020; Dill, 2015). These studies have significantly contributed to advancing our understanding of this field.

Additionally, the research landscape has been enriched by investigations covering diverse areas. Studies by Grew et al. (2019) have explored lithium mineral evolution and ecology, shedding light on the intricate relationship between lithium-bearing minerals and ecological systems. Grosjean et al. (2012) delved into the global lithium resources landscape, offering insights into the distribution and availability of this crucial element. Furthermore, other studies (McCauley and Bradley, 2014) provided an intriguing perspective by analyzing the worldwide age distribution of granitic pegmatites, offering valuable context for the geological history of these deposits.

A summary of studies using a variety of characterization methods is presented below:

- Analytical microscopy and mass spectrometry were employed to identify and characterize distinct lithium minerals in micaceous lithium-bearing ores (Aylmore et al., 2018a). The authors initially investigated various lithium mineral samples' chemical and structural attributes. They subsequently categorized and clustered different mica polymorphs by evaluating their compositions (Al/Si ratio; F, Na content), allowing them to differentiate between diverse micas with varying lithium grades.
- 2. In a recent study by Sirbescu et al. (2023), the authors proposed using in-situ trace element geochemistry and zoning patterns in spodumene to enhance the understanding of primary growth mechanisms and improve lithium extraction. The size of the giant crystals limited conventional compositional-mapping techniques. To overcome this, they introduced a two-step approach involving portable X-ray Fluorescence (pXRF) and benchtop micro-X-ray Fluorescence (µXRF) techniques. These were applied to sliced crystals, enabling 2D compositional mapping across decimeter-sized samples. Analysis of subhedral spodumene samples revealed distinct zoning patterns, suggesting two growth episodes with a change in crystallization mechanism. The integrated pXRF-µXRF method was found to aid in the compositional and alteration characterization of lithium ore, optimizing processing and extraction methods. Additionally, the technique offers new insights into chemical heterogeneities and zoning patterns within coarse to megacrystic minerals, serving as a valuable sample pre-screening method for subsequent microanalytical processes and lithium extraction procedures.
- 3. A study by Gourcerol et al. (2019) outlined vital factors contributing to lithium enrichment in rocks and minerals. These factors include a pre-existing lithium-bearing source, lithospheric thickening promoting lithium concentration, a regional or local extensional regime, and the presence of fractures facilitating exogenous processes. The authors highlighted that understanding various orogenic settings, like the Mediterranean orogens, is uneven due to insufficient exploration in this region or substantial variations in orogenic conditions.

- 4. Poellmann and Koenig (2021) proposed an alternative method for quantitatively determining lithium content in minerals, given challenges with X-ray fluorescence (XRF) and wet chemical techniques. They suggested combining X-ray diffraction (XRD) with statistical methods for more accurate results. Their approach utilized quantitative XRD, partial least square regression, and cluster analysis to identify minerals and estimate lithium content. The authors applied this method to various lithium-containing ores, such as spodumene, amblygonite, lepidolite, zinnwaldite, petalite, and triphylite. Their study achieved high detection sensitivity, with mineral content detection limits below 1% and lithium oxide detection limits of 0.1%. The researchers also discussed case studies involving complex analyses of lithium-rich salt lake brines in their paper.
- 5. Rifai et al. (2022) conducted a study using laser-induced breakdown spectroscopy (LIBS) to determine lithium concentrations and create mineralogical maps of crushed lithium ore. They examined thirty crushed ore samples (<10 mm) from a pegmatite lithium deposit. The analysis was performed using the TESCAN Integrated Mineral Analyzer (TIMA) and the LIBS ECORE analyzer to identify mineral identities and assess lithium concentrations in the samples.
- 6. Thiery and Farhat (2023) conducted a study to highlight the limitations of conventional energy dispersive spectroscopy (EDS) detectors using a lepidolite-bearing granite and a spodumene crystal. They utilized backscattered coefficient calculations to emphasize the weak contrasts observed for common lithium-bearing minerals in backscattered images. Monte Carlo simulations were employed to analyze electron-matter interactions within these minerals, providing insights into the size of the interaction zone. Their study also included simulated spectra to aid users in identifying phases of interest more effectively.
- 7. Aylmore et al. (2018b) examined different lithium minerals in spodumene-type pegmatites from the Pilbara region of Western Australia, focusing on the samples' color, texture, and various lithologies. The majority of lithium was found to be associated with spodumene particles, along with minor quantities of lithium-bearing micas and beryl. Some spodumene particles had undergone alteration in one sample, replaced by micaceous minerals like muscovite, lepidolite, trilithionite, and calcite. In contrast, the other samples generally showed spodumene particles with minimal impurities, though minor intergrowths of quartz, feldspar, and spodumene were present in coarser fractions. The study's mineralogical findings indicated that the main gangue minerals, such as quartz, K feldspar, and albite, could be removed through coarse grinding at a size of -4 mm. This process allowed for the recovery of 90% of spodumene, upgrading lithium from 0.99-1.5 wt% Li to 3.0-3.5 wt% (equivalent to 6.5-7.5 wt% Li₂O).
- 8. In a study by Aylmore et al. (2018a) in Western Australia, ore-bearing and gangue minerals were subjected to automated mineralogy techniques and analyzed using instrumentation with secondary mass spectrometry capabilities. The research aimed to determine lithium content and elemental distribution within minerals. The findings revealed that most lithium in the ore samples existed in lepidolite or zinnwaldite minerals, containing approximately 1.2-1.5% Li concentration. These minerals were composed of lithium muscovite, trilithionite, and polylithionite grains. Variability in the morphology of Li-bearing micas was observed among different deposits. Gangue materials primarily consisted of quartz and albite, constituting up to 20% of the sample. Minor amounts (about 1%) of other lithium-bearing minerals like spodumene, elbaite, and beryl were present in these samples. Lithium mica particles were sieved (4 mm

sieve) to separate them, but further grinding would be necessary to expose finer grains of lithium muscovite, polylithionite, and trilithionite for subsequent Li extraction. Breaking down micas to extract lithium would involve stabilizing and removing elements such as F, Fe, Al, Mn, K, and Na from process streams. The study also highlighted that the high concentration of Rb (0.9-3.6 wt%) and Cs (0.1-0.8 wt%) in micas makes them valuable resources for these elements, which could be recovered alongside lithium.

- 9. Other researchers (Sweetapple and Tassios, 2015) suggest that Laser-Induced Breakdown Spectroscopy (LIBS) offers an efficient and cost-effective method for qualitative and semi-quantitatively analyzing light elements, including lithium. This technique provides rapid analysis with minimal sample damage and preparation. LIBS operates on atomic emission spectroscopy, utilizing characteristic spectra emitted from plasma created by a high-energy laser pulse interacting with various sample types (solid, liquid, or gas). Their study applied LIBS mapping to hydrothermally altered spodumene samples from the Mt. Cattlin lithium pegmatite deposit in Western Australia. While spodumene is the primary ore mineral, lithium distribution extends to primary micas, tourmaline, and alteration products. The mapping effectively distinguished between spodumene, its altered forms, and matrix silicate minerals. However, quantifying LIBS results using lithium-doped borosilicate glasses as standards had limitations due to sensitivity issues and self-absorption effects at higher Li₂O values (above approximately two wt%), particularly beyond six wt%. The study demonstrates LIBS' effectiveness in mapping light elements and suggests its potential as a complementary technique to other mapping methods.
- 10. The X-ray fluorescence spectrometry (XRF) method was used in another study to determine trace amounts of lithium in mineral waters with therapeutic effects in Poland (Zawisza and Sitko, 2011). This method expands the applications of XRF to analyze very light elements. The technique involves determining lithium via iron after forming a stoichiometric potassium lithium periodatoferrate(III) complex. The resulting solution, obtained by dissolving the complex, is analyzed using XRF after pipetting it onto a Mylar foil. The method can detect as little as one microgram of lithium. Accurate determinations are achieved using simple calibration samples involving pipetting iron solution in the 8.0-28.0 micrograms range onto the Mylar foil. The thin samples eliminate errors due to self-absorption or matrix effects. The study provides crucial information about the quality of the analyzed mineral waters.
- 11. The Leinster pegmatite belt in southeast Ireland contains concealed Li-Cs-Ta albite-spodumene-type pegmatites of increasing significance for critical metals such as Li, Ta, and Be (Barros et al., 2022). In the study by Barros et al. (2022), detailed mineralogical characterization and geochemical analyses were conducted on six drill cores intersecting pegmatite bodies and their surrounding rocks. Metasomatism in the country rocks is limited to a shallow zone, implying that rock permeability influences fluid dispersion. The study suggests that halos are formed due to the release of residual fluids enriched in rare elements during the late stages of pegmatite crystallization. The geochemistry of these halos reflects the pegmatite's internal evolution, with an accumulation of incompatible elements through fractionation (Be, B, Cs, Sn, Ta) and auto-metasomatic resorption of spodumene and K-feldspar (Li, Rb). Analyzing bedrock, sediments, and soils offers a way to identify rare-element enrichment trends, providing opportunities for mineral exploration strategies in Ireland and globally for similar albite-spodumene pegmatites.

- 12. Optical and thermal remote sensing is highlighted in a review paper as a significant tool in geological exploration and lithium investigations (Cardoso-Fernandes et al., 2020). The paper covers several key aspects, such as (i) accomplishments in lithium exploration through remote sensing techniques, (ii) the primary limitations of these approaches, (iii) strategies to address these challenges, and (iv) the anticipated research directions. The authors assert that remote sensing is poised to evolve into an essential and integrated tool for lithium exploration, playing a fundamental role in the field.
- 13. Recent research has focused on lithium isotopic fractionation, a tracking technique of weathering processes. However, limited knowledge exists about the fractionation processes in highly weathered environments dominated by secondary minerals (Lara et al., 2022). This study investigated lithium isotopic fractionation in a Puerto Rican andesitic catchment known for its high silicate weathering rates. Similarly, another study examined similar objectives in the eastern Qaidam Basin of the northeastern Tibetan Plateau (Li et al., 2023). These investigations suggest that lithium is integrated into the soil matrix, offering insights into its behavior during weathering.
- 14. A newfound deposit has been the subject of a recently published paper by Sirbescu and colleagues in 2023 (Sirbescu et al., 2023). Despite years of observation and speculation, the Plumbago North deposit presents intriguing puzzles that warrant further investigation. In their study, the authors propose that insights into the primary growth mechanisms of spodumene and optimization of lithium extraction can be gleaned from in-situ trace element geochemistry and zoning patterns within the mineral. A particularly notable method employed in this research is the integrated approach of portable X-ray Fluorescence (pXRF) and benchtop micro-X-ray Fluorescence (mu XRF), which proves valuable for characterizing composition and alterations in lithium ore. This integrated method enhances understanding chemical variations and zoning patterns within coarse to megacrystic minerals. It offers the potential for effective pre-screening of samples before employing other microanalytical techniques. The study underscores the potential of this innovative approach to advance knowledge about spodumene growth mechanisms, extraction optimization, and the broader understanding of chemical variations within minerals. This multidimensional investigation holds promise for uncovering critical insights into the geological processes shaping mineral deposits like the Plumbago North deposit. Additionally, the integrated techniques open a new venue for investigating chemical heterogeneities and zoning patterns within coarse to megacrystic minerals. They may serve as an excellent sample pre-screening before other microanalytical techniques.
- 15. The challenges of lithium analysis using energy dispersive spectroscopy (EDS) are still present despite commercially available windowless detectors, which are not widespread. Since scanning electron microscopy (SEM), coupled with EDS, is the most common analytical tool in materials characterization, it is not surprising to observe an increase in the interest of Li analysis within this framework. However, there are still challenges to overcome, namely the choice of adequate analytical conditions and understanding the material behavior under the electron gun (Thiery and Farhat, 2023).
- 16. The direct determination of lithium by XRF is practically impossible due to such a light element's extremely low fluorescence yield and long-wavelength characteristic radiation.

These diverse studies, spanning various disciplines and employing various methodologies, collectively contribute to a comprehensive understanding of lithium-bearing materials, their distribution, and their significance in the broader geological and ecological contexts. In summary, adequate characterization studies are critical in the entire lithium value chain, from exploration to application. The identification of lithium-bearing minerals and the accurate determination of lithium concentration form the foundation for efficient extraction processes and informed decision-making in the field of energy-related applications. Recent research in this domain reflects the growing importance of harnessing mineral characterization for sustainable and efficient utilization of lithium resources.

2.5 Gaps and Potential Future Efforts

The development of lithium resources is a complex endeavor influenced by several critical factors. These include resource exploration, economic viability, environmental impacts, and technological innovations, particularly extraction reactions and processes. It's important to underscore that several incomplete knowledge and research areas merit future attention and efforts. Some of these critical knowledge and research gaps are highlighted below:

1. Resource occurrence, exploration, and characterization:

- a) Primary and secondary lithium resources are diverse in the United States. However, their documentation and assessment are currently inadequate, leading to an unknown amount of lithium reserves in the country. To address this, an accurate and comprehensive documentation process is crucial. Additionally, thorough characterization investigations of lithium deposits are essential to better understand their composition, size, and distribution. A focus on improving the accuracy and precision of techniques used for estimating lithium resources is also necessary. Furthermore, there's a need for primary research efforts in this field. While some standard thermodynamic parameters of lithium minerals are available, there is a lack of solubility data at different temperatures required for hydrogeochemical calculations (Boschetti, 2022). Recent attempts have been made to incorporate these parameters into the thermodynamic datasets of hydrogeochemical codes such as The Geochemist's Workbench and PHREEQC, as highlighted by Boschetti (2022). However, more extensive research is required to develop this knowledge area fully. Overall, enhancing the documentation, assessment, and understanding of lithium resources in the U.S. demands focused research efforts, ranging from detailed deposit characterization to refining estimation techniques and expanding the basic science knowledge needed for accurate hydrogeochemical calculations.
- b) Globally, studies like Gruber et al. (2011) suggest that lithium resources could be sufficient for electric vehicle (EV) batteries until the century's end. Still, uncertainties persist about meeting future energy needs and the expanding EV market. Gruber's study estimated a global lithium resource of about 39 million tonnes, with projected 2100 demand below 20 Mt. However, criticisms point out that these studies overlooked geological constraints affecting economically viable lithium production (Kesler et al., 2012), pointing out that the research needed

over the last decade aimed to gauge total lithium resources accurately, match them against demand, and address geological limitations. A recent study by Ambrose and Kendall 2020, using a resource production model and life cycle assessment, indicated global lithium resources between 293 to 527 Mt of lithium carbonate equivalent (Ambrose and Kendall, 2020). This study projected production could reach from 237,000 metric tons in 2018 to 4.4-7.5 Mt per year by 2100, with high-grade brines sustaining demand until 2035 but potentially requiring lower-grade deposits post-2050. However, despite the urgent need to satisfy the increasing demand for Li, sources of global Li production have been limited to continental brines and pegmatites (Lee, 2022). This emphasizes the importance of utilizing all available lithium resources (and new resources, petroleum source rock brines being one of them) and underscores the necessity of reevaluating the global lithium supply as new information surfaces. Persistent challenges in mining, processing, and industrial-scale recycling operations are also potential issues that were examined. Recent innovations to address these issues were introduced in a study by Tabelin and collaborators (Tabelin et al., 2021).

- Economic Feasibility and Sustainability: While studies suggest sufficient lithium resources, economic feasibility studies must account for various factors, such as fluctuating market demand, extraction costs, and potential geopolitical influences. Evaluating the sustainability of lithium extraction methods, including environmental and social impacts, remains crucial.
 - a) In a study by Kelly et al. (2021), life cycle analyses (LCAs) were conducted on battery-grade lithium carbonate and lithium hydroxide monohydrate production from Chilean brines and Australian spodumene ores. The analysis extended to include battery cathode materials and complete automotive traction batteries to assess the impact of lithium production methods on these end products. The LCA covered material, water, and energy flows throughout the supply chain, showing that lithium source differences led to up to 20% variation in greenhouse gas emissions (GHGs) for NMC811 cathode materials and up to 45% for NMC622 cathode materials. At the battery level, differences were up to 9% for NMC811 batteries and 20% for NMC622 batteries. Brine-based Li₂CO₃ and LiOH × H₂O production had lower life cycle GHG emissions and freshwater consumption than ore-based sources.
- 3. **Environmental Impact Assessment**: A thorough understanding of the environmental effects of lithium extraction and processing is required. This involves assessing the impact on local ecosystems, water resources, and greenhouse gas emissions. Research should also delve into effective mitigation strategies.
 - a) Environmental impact: The study by Xu and collaborators (Xu et al., 2023) investigated the environmental impact of lithium contamination in soil, considering its effects on soil properties and enzyme activities. Different levels of lithium treatment were applied to the ground, ranging from 10 to 1280 mg kg(-1). Results indicated that the presence of lithium led to notable increases in specific soil parameters like ammonium nitrogen, total nitrogen, and exchangeable potassium. Electric conductivity and available phosphorus content also increased

significantly, while soil pH and cation exchange capacity slightly changed. The study observed decreased nitrate nitrogen and sulfate content at higher lithium levels. Enzyme activity was influenced: lower lithium levels boosted certain enzyme activities related to carbon, nitrogen, phosphorus, and sulfur cycling, while higher levels inhibited several enzymes. The study established ecological doses (ED10 and ED50) for lithium's adverse effects on soil. Overall, the research shed light on lithium contamination characteristics in soil, aiding risk assessment and remediation strategies.

- Technological Advancements in Extraction: Developing innovative and environmentally friendly extraction methods is pivotal. Research should focus on refining extraction techniques, reducing energy consumption, and minimizing waste generation during lithium recovery.
 - a) Lithium's importance for applications like batteries and the increasing demand due to electrification and decarbonization efforts were highlighted in a recent study (Garcia et al., 2023). The supply from brines and ores might fall short of global demand unless alternative resources and efficient extraction techniques are implemented. Chemical precipitation emerged as an efficient method for extracting metals from wastewater, with the paper reviewing this technology, its challenges, and environmental impacts. The study explored alternative approaches for lithium recovery via chemical precipitation, examining the effects of various operating conditions on precipitation rates. The paper also discussed critical challenges from recent studies and implications for future innovation in lithium recovery methods.
- Battery Technology Advancements: As battery technologies evolve, research efforts should be directed toward enhancing the energy density, longevity, and recyclability of lithium-ion batteries. This includes exploring alternative materials that could replace or complement lithium in batteries.
- 6. **Circular Economy and Recycling**: Investigating efficient recycling processes for lithium-ion batteries is imperative to minimize resource depletion and waste accumulation. This involves refining techniques for recovering lithium and other valuable materials from spent batteries.
- 7. **Geopolitical Considerations**: Understanding geopolitical dynamics that could affect lithium supply chains is essential. Research should focus on potential vulnerabilities, diversification of sources, and the impact of geopolitical shifts on lithium availability.
- 8. **Social and Ethical Aspects**: Exploring the social and ethical dimensions of lithium extraction, such as community engagement, labor conditions, and indigenous rights, is becoming increasingly important.
- 9. **Integration with Renewable Energy**: As lithium-ion batteries play a crucial role in energy storage for renewable sources, research should explore synergies between lithium availability, renewable energy integration, and grid stability.

10. **Policy and Regulation**: Analyzing and formulating appropriate policies and regulations related to lithium extraction, trade, and sustainability is vital for responsible resource management on a global scale.

In conclusion, the multifaceted nature of lithium resource development demands ongoing research and collaborative efforts across various disciplines. Addressing these knowledge and research gaps is essential to ensure lithium resources' sustainable and responsible utilization in the evolving energy landscape.

2.6 Processing and extractions methods/technologies

vehicles and grid storage, has led to a substantial increase in interest and research focus on lithium recovery and extraction. While lithium from brines has been the primary source, attention has focused on lithium-bearing minerals due to their wider availability and quicker market access, with several new industrial projects launched and various novel methods proposed (Li et al., 2019).

The Scopus database recorded around 13,000 scientific publications on this topic in 2021, reflecting the urgency of addressing this critical issue. The uneven distribution of lithium mineral resources across countries and the varying lithium concentration in brine reserves underscore the significance of efficient lithium extraction methods (Meng et al., 2021).

The existing knowledge about lithium extraction from minerals is dispersed across various sources, including patents, journal articles, and proceedings. This fragmentation emphasizes the need for comprehensive reviews to thoroughly understand the spodumene phase system, phase conversion processes, and the intricacies of lithium extraction (Dessemond et al., 2019).

The contemporary methods of lithium recovery primarily involve minerals, especially spodumene, and encompass acid, alkaline, and chlorination processes (Meng et al., 2021). Lithium extraction from brines is also achieved through crystallization, solvent extraction, and ion exchange processes. This diverse range of extraction methods emphasizes the multifaceted approaches required to effectively recover lithium from various sources. Present endeavors are directed toward enhancing lithium extraction technologies, exploring recycling alternatives, and investigating novel sources like geothermal brines and seawater. These efforts aim to ensure a sustainable supply of this essential metal to meet the growing demand of the lithium-ion battery industry.

2.6.1 Brief description of current methods

Summaries of recent studies that describe methods to separate lithium-bearing minerals and compounds are provided below:

 Aylmore et al.'s (2018b)study focused on mineralogical observations related to the recovery of spodumene, an essential lithium-bearing mineral. The study found that the main gangue minerals, including quartz, K feldspar, and albite, can be effectively removed at a coarse grind size of -4 mm. This removal process enables the recovery of 90% of spodumene, corresponding to an increase in lithium content from 0.99-1.5 wt% Li to 3.0-3.5 wt% (equivalent to 6.5-7.5 wt% Li₂O). Further particle size reduction is suggested to enhance the recovery of spodumene from the coarse fractions. This reduction would help separate spodumene from micas and feldspars. However, the need to remove mineral impurities from spodumene in downstream processing depends on the processing method. Lithium-bearing micas, calcite, and feldspar can positively or negatively impact lithium recovery, highlighting the complexities of efficient spodumene processing.

- 2. The article by Kundu et al. (2023) addresses the surging demand for lithium in the energy sector. It focuses on using pegmatites as a significant lithium resource. Within pegmatites, spodumene is highlighted as the primary lithium-bearing mineral. The article provides a comprehensive overview of research investigations and operational practices concerning diverse techniques for extracting lithium from pegmatites. It delves into these techniques and encompasses the global distribution of spodumene-bearing pegmatite occurrences. The article examines explicitly the beneficiation of spodumene using Dense Media Separation (DMS) and froth flotation, widely adopted techniques in the field. Additionally, it explores the application of magnetic separation and ore sorting methods in spodumene processing. Furthermore, the article addresses the postbeneficiation steps required to transform the spodumene concentrate into marketable lithium-based salts. This involves additional treatment involving heat and acidic or alkaline media. The report comprehensively reviews various pyrometallurgical and hydrometallurgical routes employed in processing spodumene to generate lithium-based salts suitable for market consumption. The article offers a comprehensive overview of the entire process chain of lithium recovery from spodumene-bearing pegmatites. It covers techniques for beneficiation, processing, and transformation into usable lithiumbased salts, thus contributing to a holistic understanding of the extraction and processing of lithium from pegmatite resources.
- 3. The review by Tadesse et al. 2019 centers on lithium extraction from hard rock pegmatite ores, primarily emphasizing spodumene, the main lithium-bearing mineral. The review delves into various techniques for beneficiating lithium minerals from these hard rock ores. It highlights two main methods: dense media separation and flotation, which separate lithium minerals from the ore. Several factors are discussed as critical in lithium minerals flotation, including the surface chemistry of minerals, choice of collector, pulp pH, chemical pre-treatment methods, and the presence of slimes. Additionally, the review provides insights into the beneficiation flowsheets implemented in some of the world's larger lithium processing plants. This comprehensive overview of lithium extraction techniques from hard rock pegmatite ores is valuable for researchers and industry professionals.
- 4. In a study by Sandmann and Gutzmer (2011), two mineral processing methods were evaluated for treating a bulk sample of lithium-bearing topaz-mica-greisen from Zinnwald, Eastern Erzgebirge, Germany (Sandmann and Gutzmer, 2011). The methods tested were conventional mechanical breakage and electrical comminution. Mechanical breakage involved crushers and mills, while electrical fragmentation was conducted using a selFrag Lab system. The resulting products were subjected to magnetic separation for concentration, and all materials were analyzed using mineral liberation analysis (MLA). The concentrates obtained through magnetic separation showed significant enrichment in zinnwaldite, a lithium-rich mica, reaching concentrations of 95 to 97 wt%. The study's findings from mineral association analyses using MLA revealed

that Li-micas treated with the selFrag system exhibited slightly improved liberation than those processed conventionally.

Literature resources covering lithium extraction methods from minerals, brine, and other resources are included below.

- 1. The literature review by Dessemond et al. (2019) provides a comprehensive overview of the lithium industry, encompassing various aspects such as the lithium market, global resources, and the production processes of lithium compounds. The primary focus is on the production of lithium compounds from spodumene minerals. Spodumene is known for its elevated lithium content and efficient extraction capabilities. Given the dispersed nature of data regarding lithium extraction from minerals across patents, journal articles, and proceedings spanning several years, the review seeks to fill this gap by conducting a thorough examination. This encompasses an in-depth exploration of the spodumene phase system, phase conversion processes, and the methods employed for extracting lithium. By consolidating and analyzing this scattered information, the review aims to provide a coherent understanding of the processes involved in producing lithium compounds from spodumene minerals, thus contributing to the broader understanding of the lithium industry's complexities and advancements.
- 2. The study conducted by Qiu et al. (2023) focuses on refining the conventional process of lithium extraction from alpha-spodumene, which typically involves high-temperature calcination to convert alpha-spodumene to beta-spodumene, followed by concentrated acid roasting and water leaching. The study proposes an alternative approach to directly prepare water-soluble lithium salts from alpha-spodumene through roasting with various sulfates. The goal is to eliminate the need for concentrated acid and simplify extraction. The study introduces an innovative approach to lithium extraction from alpha-spodumene by utilizing sulfate roasting to produce water-soluble lithium salts. This approach eliminates the need for concentrated acid and offers potential simplification of the extraction process, contributing to lithium production and processing.
- 3. In a study by Ryabtsev (2005), a relentless sorption beneficiation technology was developed for hydrogenic mineral products containing lithium, specifically calcium chloride and magnesium chloride compounds (Ryabtsev, 2005). This technology enables the extraction of lithium concentrates with a significantly reduced ratio of combined magnesium and calcium concentration to lithium concentration, reaching less than 15. This ratio is notably lower, about 12-25 times, compared to the primary brines used in the process.
- 4. In the study by Schneider et al. (2017), the increasing importance of lithium as an energy-critical element and the need for a secure supply prompted attention towards the mica-type mineral zinnwaldite as a potential local German resource. Zinnwaldite is a lithium-rich siderophyllite and corresponds to an intermediate polylithionite siderophyllite solid solution with elevated fluoride content. Mineral samples from the Zinnwald/Cinovec deposit along the German/Czech border were extensively analyzed and characterized, focusing on their thermal behavior. Gaining insight into the mineral's thermal properties offers the opportunity to develop new and cost-effective methods for lithium extraction.

Various spectroscopic techniques were used to investigate the decomposition mechanisms. Oxidation of Fe^{2+} triggered dehydroxylation via dehydrogenation, commencing at 300 degrees C. This was followed by a dehydroxylation process akin to that of dioctahedral micas. Elevated temperatures led to hydrogen fluoride (HF) release, with hematite precipitation observed at around 800 degrees C. Complete zinnwaldite decomposition occurred at 900 degrees C, liberating SiF₄ and producing several solid decomposition products. Single-crystal diffraction utilizing X-rays and neutrons identified structural changes post-annealing at 700 degrees C. These results indicated a transformation into a polylithionite-like structure, representing the end member of the solid solution series.

- 5. In the study by Wang et al. (2022), the increasing prevalence of electronic devices equipped with lithium-ion batteries has raised concerns about the sustainability of relying solely on limited land-based lithium resources to meet growing market demand. Due to their abundant reserves and cost-effectiveness have led to a global interest in recovering lithium from alternative sources such as salt-lake brines, geothermal brines, battery waste treatment wastewater, and even seawater. Due to secondary pollution, traditional methods like solar evaporation-precipitation are time-consuming and environmentally problematic. Recently, electrochemical technologies have gained significant attention for lithium recovery due to their efficiency, environmental benefits, and shorter processing times. The study outlines the progress made in lithium recovery using electrochemical technologies, discussing principles, advantages, and challenges based on previous literature. While these methods are technically feasible, their application on a large scale is hindered by technical immaturity. The authors emphasize the need for future efforts to enhance electrochemical technologies by improving lithium selectivity, material stability, and energy efficiency while reducing costs. Such advancements would guide the development of more effective electrochemical methods for lithium recovery from liquid resources, thereby enabling a sustainable and renewable society.
- 6. The study by Li et al. (2019) reviewed state-of-the-art lithium recovery methods from various mineral resources. It highlighted significant lithium deposits' abundance and global distribution. Different recovery methods for minerals like spodumene, lepidolite, zinnwaldite, amblygonite, and clays are summarized and discussed. The paper predicted that spodumene would continue being dominantly used as a lithium resource over other minerals and with sulfuric acid roasting as a significant processing method. However, future research trends include direct processing of spodumene and LiOH production. Fluoride-based plans show promise but require further investigation for sustainability. Efficient utilization of valuable elements in lepidolite and zinnwaldite is essential to compete with spodumene. Additionally, the study emphasizes the importance of managing waste and downstream purification steps in the lithium recovery process. Overall, this review provides insights into the development of Li recovery from mineral resources.
- 7. The paper by Liu et al. (2023) underscores the pivotal role of lithium as the most crucial energy metal in the 21st century, with a demand that has surged significantly over the past decade and it is expected to continue growing (Liu et al., 2023). Given the limited availability of lithium on the market, extracting lithium from natural sources remains the

preferred choice for rapidly evolving industries. This review focuses on recent technological advancements in lithium extraction from natural resources. It categorizes existing methods according to the primary sources, such as spodumene, lepidolite, and brine. The paper meticulously compares the advantages and disadvantages of each extraction method. Furthermore, it offers valuable recommendations for the future development of lithium extraction from natural sources based on a comprehensive understanding of the current methodologies. This review is a useful reference for research, development, optimization, and industrial implementation of future lithium extraction processes and methods, addressing the growing demand for this critical energy metal.

- 8. In a study by Martin et al. (2017), a process for producing lithium carbonate using supercritical carbon dioxide (sc-CO₂) treatment was developed and optimized based on decomposition studies of zinnwaldite. The process involved subjecting sintered and ground zinnwaldite concentrate to treatment with CO₂ and water at elevated pressure (100 bar) and moderate heating (230 degrees C). This treatment resulted in mobilization rates of over 70%. The lithium bicarbonate-containing solution obtained from the process was then concentrated through electrodialysis, achieving a lithium content of 8.5 g/L. Lithium carbonate precipitation was carried out by eliminating CO₂ at temperatures between 90-95 degrees C. Notably, the process exhibited high selectivity for alkali metals, particularly lithium, allowing lithium carbonate production with purities reaching 99.0% without additional rinsing steps. This research offers a promising method for efficient lithium carbonate production.
- 9. The study by Zhao et al. (2023) highlights the increasing strategic importance of metallic lithium in various industries, resulting in a growing demand for Li-related resources. Specifically, the study focuses on lithium-bearing clay minerals found in nature, including lepidolite (polylithionite and trilithionite), zinnwaldite, masutomilite, swinefordite, hectorite, cookeite, and jadarite). These minerals have relatively simple structures and are widely distributed in Asia and America, making them valuable Li resources. The review provides insights into the structures and properties of lithium-bearing clay minerals and evaluates five extraction methods, focusing on the advantages and deficiencies of the extraction methods. It concludes that these clay minerals typically possess a 2:1 layered structure, with Li⁺ ions capable of entering the interlayer spaces and becoming fixed within the mineral crystals through mineralization or isomorphism. Among the extraction methods, acidification emerges as a mature technique with the potential for low energy consumption and high extraction efficiency. Consequently, acidification is the primary method for extracting lithium from clay minerals. However, the study highlights the need for further improvement, including understanding reaction mechanisms, process optimization, equipment design, reagent recovery, and waste disposal. In addition to extraction, the study emphasizes the importance of the safe treatment and potential reuse of residue and waste in future recovery methods. Overall, this review provides valuable information on lithium extraction from clay minerals and offers insights into efficient extraction methods.
- 10. The study by Caciagli et al. (2011) investigates the behavior of lithium under high temperatures and pressures in geological conditions. They measured how lithium partitions between different minerals (clinopyroxene, olivine, plagioclase) and hydrous

fluid at temperatures ranging from 800 to 1100 degrees Celsius and a pressure of 1 gigapascal (GPa). The study found that lithium behaves mildly incompatible in the solid minerals compared to the fluid phase, similar to its behavior in mineral-melt systems. Specifically, they observed that the partitioning of lithium between clinopyroxene and fluid, as well as between olivine and liquid, decreases as temperature increases. The chemical composition of the minerals also influenced the partition coefficients of lithium. Higher aluminum (Al₂O₃) content in clinopyroxene and higher iron oxide (FeO) content in olivine increased the partition coefficients, while higher plagioclase content decreased them. The study also examined the isotopic fractionation of lithium between clinopyroxene and fluid, finding that it varied within a range from -0.3 to -3.5 parts per thousand. Overall, the research suggests that in geological processes involving the movement of fluids through rocks, lithium is rapidly exchanged with the surrounding mantle, which tends to buffer the fluid's lithium composition toward values typical of the cover. As a result, the distinctive lithium signature associated with subducting slabs is attenuated when fluids migrate through porous media. For the preservation of a slab-like lithium signature, more specialized fluid transport mechanisms, such as fracture flow, would be necessary to transfer the signature from the subducting slab to the source of island arc basalts.

- 11. The paper by Cook and Gibson (2023) addresses the increasing demand for lithium-ion batteries, which has led to numerous lithium mineral projects worldwide. However, these projects face significant mineral processing challenges, including the similarity in behavior between gangue minerals and valuable lithium minerals and issues related to poor selectivity in froth flotation processes. In spodumene flotation, the primary collectors used are unsaturated anionic fatty acids. These collectors are known to be firm with poor solubility and selectivity. The consensus in fundamental flotation research suggests that spodumene flotation is driven by the formation of a complex between the fatty acid collector and anions adsorbed at cationic aluminum sites. Despite this understanding, many small-scale studies have reported suboptimal recoveries in spodumene flotation. This has prompted researchers to explore alternative approaches, such as using cationic activators or mixed anionic/cationic collectors to enhance flotation performance. One notable aspect highlighted in the paper is the scarcity of testwork using actual spodumene ore in recent literature. Older publications from various deposits have demonstrated that fatty acids can effectively concentrate spodumene. The typical process involves alkaline scrubbing, high-density fatty acid conditioning, and flotation at pH levels between 7.5 and 8.5, with a collector concentration of 500-750 g/t fatty acid. However, the collector's behavior is sensitive to pulp conditions around this pH range, potentially leading to unstable flotation circuits and inconsistent results. In summary, the paper reviews the properties of fatty acid collectors and compiles existing industrial and fundamental research on spodumene flotation. The goal is to provide new insights into the interactions between particles and collectors in spodumene flotation and to bridge the gap between fundamental understanding and industrial processes. This knowledge is crucial for de-risking projects in the growing lithium mineral industry.
- 12. The paper by Gmar and Chagnes (2019) discusses the rapidly growing importance of lithium, particularly in the context of the electric vehicle industry. There is a pressing need to develop sustainable and cost-effective methods for extracting lithium from

primary and secondary sources to meet the expected global demand for lithium. One promising technology highlighted in the paper is electrodialysis, considered an attractive alternative for producing lithium from various sources, including brines, ores, and spent lithium-ion batteries, through a hydrometallurgical process. Electrodialysis has primarily been used at an industrial scale for water treatment applications, but it holds significant potential for the future of lithium production. The paper provides an overview of recent advancements in electrodialysis technology and its potential role in the next generation of lithium production processes. This suggests that electrodialysis could be a valuable asset in addressing the increasing demand for lithium while contributing to sustainable and economical lithium recovery methods.

- 13. The review by Hu et al. (2020) discusses the crucial role that the exploitation and utilization of mineral resources have played in China's rapid economic development. Despite the long history of mineral processing, the technologies in this field have evolved in response to changing market demands, particularly for minerals with diminishing high-grade deposits. The review focuses on the efforts made by the authors in developing new approaches for the utilization of low-grade minerals, with a specific emphasis on iron ores and lithium-containing brines. This emphasis is justified by the significance of iron in modern civilization and the importance of lithium as a critical component in electric vehicles for transportation. Additionally, the review covers utilizing magnesium chloride reserves, one of western China's most extensive waste materials. These reserves are explored as potential raw materials for the fabrication of functional materials. In summary, the review highlights the ongoing efforts to find innovative and sustainable ways to utilize low-grade minerals, recognizing their importance in various industries and the need to adapt to changing resource availability and market demands.
- 14. In the study by Aylmore et al. (2018), it was observed that most lithium mica particles were separated from the primary gangue minerals when the samples were treated and screened to pass through a 4 mm sieve. However, it was noted that further grinding would be necessary to break up and expose the refined grains of Li-bearing minerals such as muscovite, polylithionite, and trilithionite. This additional grinding step is essential to facilitate lithium extraction from these minerals. Moreover, the processes used to break down the mica minerals for lithium extraction would also require efforts to stabilize and remove various impurities, including fluorine (F), iron (Fe), aluminum (AI), manganese (Mn), as well as monovalent ions like potassium (K) and sodium (Na) from the process streams. The presence of these impurities needs to be minimized to obtain high-purity lithium compounds. One exciting aspect highlighted in the study is that the high concentrations of rubidium (Rb) and cesium (Cs) in the mica minerals (0.9-3.6 wt% Rb and 0.1-0.8 wt% Cs) make mica a favorable resource for these elements as well. This suggests that, in addition to lithium, it is possible to recover Rb and Cs during the lithium extraction process from these mica minerals.

Other papers that discussed methods of extracting lithium from seawater are:

 In the study by Liu et al. (2020), developing efficient methods for extracting lithium directly from seawater is a compelling goal to ensure a stable supply of this resource. However, seawater's high sodium (Na) concentration presents a significant challenge for

Li extraction. To address this, the researchers introduced innovative electrochemical intercalation techniques using TiO₂-coated FePO₄ electrodes. These pulsed-rest and pulse-rest-reverse pulse-rest were designed to mitigate intercalation overpotential and enhance Li selectivity. The pulse-rest-reverse pulse-rest approach was particularly noteworthy as it improved Li selectivity and contributed to maintaining the stability of the electrode's crystal structure during the co-intercalation of Li and Na. This stability enhancement resulted in a prolonged electrode lifetime. The study successfully demonstrated the extraction of Li from authentic seawater over ten cycles, achieving a Li-to-Na recovery ratio of approximately 1:1, equivalent to a selectivity of around 1.8 × 10⁴. Furthermore, using lake water with a higher initial Li/Na ratio, the researchers achieved Li extraction with a remarkable Li-to-Na recovery ratio of more than 50:1. Overall, Liu et al. (2020) introduced innovative electrochemical techniques utilizing TiO₂coated FePO₄ electrodes for efficient Li extraction from seawater, overcoming the challenge posed by the high Na concentration. Their approach showed promising results, including enhanced Li selectivity, improved crystal structure stability, and successful Li extraction from seawater and lake water sources.

Methods of extraction of lithium from salt-lake brines are included in the following publications.

- 1. The review paper by Liu et al., 2019 discusses the growing interest in extracting lithium from salt-lake brines due to their abundant reserves and increasing demand (Liu et al., 2019). The review covers various aspects, including lithium demand, available resources, processing methods, and challenges. It also details their principles and operations, detailing advancements in solvent extraction, ion-sieve adsorption, electrochemical approaches, and membrane technology. Additionally, promising techniques like ion-sieve modification, rocking-chair batteries, and liquid-membrane electrodialysis are discussed for their effectiveness in separating lithium from other ions. The paper concludes that a successful and sustainable lithium extraction process from brines will require integrating multiple recent technologies.
- 2. The paper by Stempkowska (2021) focuses on analyzing natural mineral alkali fluxes used in typical mineral industry processes. The primary goal is to reduce the melting temperature of these flux systems. The paper pays particular attention to lithium aluminum silicates and their potential to simplify and speeding up heat treatment processes. Specifically, the report examines an alkaline flux system that incorporates lithium. The study investigates a fundamental flux system that relies on sodium, potassium, and lithium aluminosilicates. By utilizing naturally occurring raw materials like spodumene, albite, and orthoclase, the researchers aim to achieve the eutectic composition with the lowest melting point. The study results indicate the presence of two eutectic pieces, mainly when the system contains approximately 30% spodumene. The paper also highlights the significant influence of sodium feldspar in these systems.
- 3. The paper by Zhang et al. (2019) highlights the significance of lithium as a crucial raw material for various industries, including glass, ceramics, nuclear materials, pharmaceuticals, and batteries. It emphasizes that about 80% of the world's lithium reserves are found in salt-lake brines, making it essential to extract lithium from these

sources to meet industry demands. The paper reviews different methods for lithium extraction developed over the years, such as precipitation, ion exchange, adsorption, solvent extraction, and electrolysis. Among these methods, precipitation is the oldest and has several advantages, including low cost, adherence to green principles, and ease of industrialization. The paper focuses explicitly on precipitation technology for lithium extraction, discussing its mechanisms and key parameters like precipitant dosage, pH value, temperature, and particle size of the precipitate. It also explores various extraction methods' economic and environmental aspects and suggests potential technologies. Additionally, the paper introduces novel magnesium precipitants as a promising approach for extracting lithium from brines with high magnesium-to-lithium mass ratios. This technology offers potential benefits for fully utilizing lithium and magnesium resources. The paper concludes by proposing various precipitation approaches for lithium extraction from brines and suggests areas for further research and investigation in this field.

- 4. The paper by Yelatontsev and Mukhachev (2021) highlights the growing demand for lithium (Li) and its compounds, with a 10% increase over the past decade. It notes that lithium's production and industrial use indicate advanced countries' innovative potential. Despite Russia's large-scale and high-quality lithium deposits in regions like Kola and Irkutsk, most lithium production relies on imports. The paper discusses the prevailing methods for lithium production in modern Russian contexts, which involve roasting and hydrometallurgical processing of ores and concentrates using sulfuric acid and limesoda methods. It comprehensively reviews lithium production technologies from industrial sources such as spodumene, lepidolite, petalite, and mica. The significant methods currently used in Russia, Kazakhstan, and Ukraine are compared with global scientific advancements, offering insights into the current state of technology. The paper emphasizes that the sulfation method, with recent enhancements, has significantly improved its technological efficiency. Sulfuric acid treatment of spodumene is highlighted as the most cost-effective approach for processing lithium ores containing at least 1.0% Li₂O without prior enrichment. Lime roasting is also discussed, emphasizing its versatility, use of readily available reagents, and direct production of lithium hydroxide from raw material. However, it has its drawbacks, including the need for high lithium content in concentrates and increased energy consumption. The paper briefly explores autoclave leaching methods for Ukrainian petalite ores, which are optimal for the highly efficient processing of low-grade raw materials. It also touches upon lithium-mica processing, waste disposal, and economic considerations. In conclusion, the paper provides an overview of industrial technologies for processing lithium ores and concentrates, primarily used in Eastern Europe and Russia, shedding light on the current state of lithium production in the region.
- 5. A novel approach for extracting lithium from minerals in aqueous solutions was recently developed (Wang et al., 2023). A phenolic resin-supported H₂TiO₃ foam (RF/UF-HTO) was made for this purpose. Key findings were that the thermosetting phenolic resin was modified with urea and then foamed using petroleum ether with boiling points ranging from 60 to 90 degrees Celsius in a mixture of 1.5% Tween 80 and 3% sodium dodecyl sulfate. This process resulted in a material with a porous 3D network structure, high specific surface area, and porosity. The material exhibited a high adsorption capacity for

Li⁺, with a maximum capacity of 52.41 mg/g. Adsorption was controlled by particle diffusion, which was determined to be an endothermic process through microcalorimetry. The material showed excellent adsorption performance for low-concentration Li⁺ in geothermal water with low mineralization. After only 6 hours, the adsorption capacity reached 21.50 mg/g, and even after ten cycles, there was only a slight attenuation in adsorption capacity (1.96 mg/g). However, in the case of salt lake brine, which had high magnesium concentration and mineralization, the adsorption capacity for Li+ was initially low. However, this challenge was effectively addressed by regenerating the material with Ba(OH)₂. This regeneration process enhanced the adsorption capacity from 0.54 to 20.72 mg/g. The material maintained a high adsorption capacity, reaching 8.5 mg/g even in fixed-bed adsorption experiments. Based on these promising properties and results, the developed material and method hold the potential for efficient Li⁺ recovery from brine with varying degrees of mineralization and composition, making it a valuable contribution to lithium extraction from liquid mineral sources.

- 6. In the study by Brandt and Haus (2010), a new concept for the enrichment of lithium minerals was proposed, aiming to achieve higher purity and higher yield by applying innovative processing technologies tailored to the specific properties of pegmatitic host rocks. The key points highlighted in this concept are as follows: 1.) The new processing concept is designed to enhance the purity and yield of lithium minerals, addressing the unique characteristics of pegmatitic host rocks. This approach aims to optimize the extraction process for lithium. 2.) The concept also emphasizes creating additional value from high-quality by-products. These by-products are expected to contribute to the sustainability of mining activities and help reduce overall production costs. 3.) In cases where traditional flotation methods are not applicable, the new concept explores alternative wet separation techniques. It suggests that flotation may even be avoided in some instances. 4.) Electrodynamic fragmentation and optical sorting are two innovative processing technologies central to this new concept. These technologies are integrated to achieve highly selective liberation and separation processes for lithium minerals. 5.) The study presents detailed results of laboratory-scale tests, demonstrating the feasibility and effectiveness of the new process design. These tests indicate that the concept can achieve selective liberation and separation of lithium minerals. 6.) Optical and mineralogical analyses of the test products suggest that the new processing concept holds significant promise for commercial applications. It offers the potential for improved efficiency and purity in lithium mineral extraction. In summary, the study introduces a novel approach to the enrichment of lithium minerals tailored to pegmatitic host rocks. It combines innovative processing technologies to achieve higher purity and yield while generating by-product value. The concept can potentially enhance the sustainability and cost-effectiveness of lithium mining operations.
- 7. The Butylskii et al. (2023)review highlights the ongoing efforts to develop more costeffective and environmentally friendly membrane technologies for lithium recovery, aiming to replace traditional reagent-based methods. Here are the key points from the review: 1.) Many researchers are working on improving lithium recovery methods to make them more economically viable and environmentally safe. The primary focus is membrane technologies as an alternative to chemical-based methods. 2.) The review comprehensively overviews traditional and innovative lithium recovery methods. It

covers the extraction of lithium from natural sources and leachates produced during the disposal of spent batteries. 3.) The primary emphasis is membrane methods, considered promising for lithium recovery. Various membrane approaches are discussed, classified, and analyzed. 4.) The review delves into practical and theoretical membrane-based ion separation. It explores the separation mechanisms and mathematical models used in these processes. 5.) The review focuses on pressure-driven and electromembrane processes, which have seen significant development at the laboratory level. These processes are beneficial for extracting lithium and other singly charged ions from mixed solutions containing high concentrations of magnesium and calcium. 6.) The review compares the results obtained from commercial membranes with those from laboratorymade membranes. This comparison provides insights into the effectiveness of different membrane materials. 7.) The review discusses novel and emerging approaches for effectively separating lithium ions from mixtures containing singly charged cations. This includes hybrid electrobaromembrane methods. In summary, the review provides a comprehensive overview of membrane-based technologies for lithium recovery, emphasizing their potential to replace traditional reagent-based methods. It covers various aspects of these technologies, from experimental and theoretical considerations to emerging approaches, making it a valuable resource for researchers and specialists in lithium recovery.

8. In the study by Martin et al. (2017), the researchers developed and optimized a process for producing lithium carbonate using supercritical carbon dioxide (sc-CO₂) treatment. Here are the key findings from their work: 1.) The starting material for lithium carbonate production was sintered and ground zinnwaldite concentrate, a mineral containing lithium. 2.) The zinnwaldite concentrate was subjected to CO₂/water treatment under elevated pressure (100 bar) and moderate heating (230 degrees Celsius). This treatment process led to the mobilization of lithium from the mineral. 3.) The researchers achieved mobilization rates of over 70%, indicating the efficient extraction of lithium from the zinnwaldite concentrate. 4.) The filtered solution containing lithium bicarbonate was then concentrated using electrodialysis, resulting in a solution with a lithium content of 8.5 g/L. Subsequently, lithium carbonate was precipitated from this concentrated solution by eliminating CO₂ at temperatures ranging from 90 to 95 degrees Celsius. 5.) The study demonstrated that the CO₂ treatment process exhibited high selectivity for alkali metals, particularly lithium. This selectivity allowed for lithium carbonate production with a high purity of 99.0% without additional rinsing or purification steps. In summary, Martin et al. successfully developed and optimized a process for lithium carbonate production using sc-CO₂ treatment of zinnwaldite concentrate. The process resulted in high lithium mobilization rates, efficient concentration, and the production of high-purity lithium carbonate. This research contributes to lithium's efficient extraction and purification, a critical element in various industries.

2.6.2 Gaps and potential future methods/technologies

To achieve lithium independence in the United States, it's crucial to address gaps in current lithium extraction methods and explore potential future technologies for extracting lithium from various resources. Here's a pathway to achieving US lithium independence:

Resource exploration includes conducting comprehensive surveys to identify and evaluate lithium deposits of all types, particularly in regions with historically unexplored or underexplored lithium resources. Geological surveys and exploration initiatives should be encouraged and supported.

Increased support for research efforts, especially efforts to develop and optimize extraction methods for different (and all) lithium resources. Improving extraction processes' efficiency, decreasing environmental sustainability, and increasing cost-effectiveness are all important.

Develop advanced lithium extraction technologies. A recent paper provides a comprehensive review of lithium recovery processes that have already been studied and are currently in industrial practice, hoping to provide some inspiration to explore new technologies for the sustainable recovery of lithium from minerals, brines, and LIBs (Meng et al., 2021). These authors claimed lithium is mainly recovered from minerals (especially spodumene) by acid. alkaline, and chlorination processes and from brines by crystallization, solvent extraction, and ion exchange processes. Other authors have emphasized that the close similarity in chemical and physical properties between lithium minerals and associated gangue minerals complicates the beneficiation of lithium minerals from ores (Tadesse et al., 2019). The chemical and physical properties similarity between lithium minerals and associated gangue minerals complicates separating lithium-bearing minerals. Factors like mineral surface chemistry, collector type, pH, chemical pre-treatment techniques, and the presence of slimes are crucial in lithium mineral flotation. Issues with separating lithium-bearing minerals from rock/mixtures of minerals remain. A recent study suggested further particle size reduction to enhance the recovery of spodumene from the coarse fractions (Aylmore et al., 2018b). According to these authors, this reduction would help separate spodumene from micas and feldspars. However, the issue is that the need to remove mineral impurities from spodumene depends on the processing method. In addition, lithium-bearing micas, calcite, and feldspar can positively or negatively impact lithium recovery, highlighting the complexities in achieving efficient spodumene processing. In addition, according to Tadesse et al. (2019), spodumene from pegmatite deposits is currently expected to be the primary source of lithium from ores, although future sources would include other minerals such as lepidolite, petalite, zinnwaldite, jadarite, and hectorite. The question is, what would be the challenges to extracting lithium from these other minerals? Advanced lithium extraction methods should be developed; a few ideas follow:

Methods to remove mineral impurities from mixtures of minerals and rock and separate lithium-bearing minerals, e.g., spodumene, need further improvement. The presence of other minerals such as micas, calcite, and feldspar can either positively or negatively impact lithium recovery, highlighting the complexities in achieving efficient spodumene processing. In addition, studies have emphasized the role of several critical factors in lithium minerals flotation, such as surface chemistry of minerals, choice of collector, pulp pH, chemical pre-treatment methods, and the presence of slimes. The separation methods should consider all these factors during method optimization efforts.

Future efforts are also needed to enhance electrochemical technologies by improving lithium selectivity, material stability, and energy efficiency while reducing costs.

In the case of lithium-bearing brines a successful and sustainable lithium extraction process from brines will require integrating multiple recent technologies.

Direct Lithium Extraction (DLE): Investigate and develop DLE technologies, which offer a more efficient and environmentally friendly way to extract lithium from brines without requiring extensive evaporation ponds. Techniques like adsorption, ion exchange, and membrane-based separation methods hold promise.

Hydrometallurgical Innovations: Research innovative hydrometallurgical processes that reduce the environmental impact of lithium extraction from minerals like spodumene and petalite.

Electrochemical Extraction: Explore electrochemical methods that selectively extract lithium from various raw materials. This includes the development of new electrode materials and cell designs.

Bioleaching: Investigate the potential of using microorganisms to extract lithium from ores and concentrates, which could be an environmentally friendly approach.

Recycle existing batteries: Promoting lithium-ion battery recycling and the second-life use of batteries in energy storage applications is essential. This approach can contribute to a sustainable lithium supply chain while reducing the need for primary extraction. The recycling process consists of dismantling the LIBs, in some cases separating the cathode and anode materials, leaching shredded material, and separating and recovering metals (Meng et al., 2021). Nonetheless, the industry standard for recycling LIBs is the pyrometallurgy processes, primarily focused on recovering base metals, such as cobalt and nickel, rather than lithium. Varying compositions of batteries for different applications require developing a suitable and sustainable recycling process to recover metals from all types of LIBs.

Work is also needed to establish policies and incentives to encourage domestic lithium production. This may include tax incentives for lithium mining companies, research grants for lithium extraction technologies, and regulations that promote responsible lithium mining and processing. Also, explore 6. International partnerships should be explored to help secure a stable lithium supply while reducing dependence on a single source.

By implementing these steps and fostering innovation in lithium extraction technologies, the United States can work toward achieving lithium independence while minimizing environmental impact and promoting economic growth in the clean energy sector. Collaboration between government, industry, and research institutions is essential to realizing this vision.

3<mark>.⊕</mark>Summary

Lithium is gaining prominence as a critical element in transitioning to eco-friendly energy production and reducing dependence on fossil fuels. Exploitable lithium deposits have been discovered globally, with estimates reaching 89 million tons. In the United States, there are approximately 20 sites containing significant lithium resources, primarily from continental brines, pegmatites, geothermal brines, hectorite, oilfield brines, and searlesite, totaling 9.1 million tons. Previously, the U.S. heavily relied on lithium imports, mainly from Chile and Argentina. However, there has been a push to develop domestic lithium sources. Of note are the McDermitt Caldera (aka Thacker Pass, Clayton Valley) for lithium ores and the Salton Sea for lithium brines. Numerous other exploration projects and initiatives across the United States seek to identify and develop new lithium resources to meet the growing domestic and global demand. These projects are at various stages of development, ranging from initial exploration to advanced stages, awaiting necessary approvals and financing.

Various geological settings contribute to lithium production, including lithium-rich brines, pegmatites, and clay deposits. Pegmatites are particularly significant, with spodumene as a primary source. Complex geological processes and tectonic dynamics influence the formation of economically crucial pegmatites. Lithium distribution is diverse, occurring in different geological contexts, such as LCT granitic pegmatites, highly peralkaline pegmatites, metasomatic rocks, and manganese deposits.

With escalating lithium demand due to EV and grid storage growth, research on lithium recovery and extraction from both brine reserves and lithium-bearing minerals is intensifying. The focus on minerals like spodumene is because of their availability and quicker market access. Approximately 13,000 publications to date highlight this surge in research. Knowledge about lithium extraction is dispersed among patents, journals, and proceedings. This fragmentation necessitates comprehensive reviews to fully understand the extraction intricacies, the spodumene phase system, and phase conversion processes. Notable methods include spodumene recovery, pegmatite extraction, electrical comminution & and mechanical breakage, alpha-spodumene processing, hydrogenic mineral products, Zinnwaldite processing & and electrochemical technologies, and multiple methods of lithium Extraction from clay minerals, sea/salt water, oil-produced water, and geothermal sources.

3.1 Challenges

Despite the abundant resources, the lithium production industry in the US faces challenges such as stringent environmental regulations, lengthy permit processes, and competition from international producers. The need for substantial investment in infrastructure, technology, and skilled labor is also a significant barrier to rapidly scaling up production.

With lithium being a critical component for the burgeoning EV and renewable energy sectors, developing and exploiting lithium resources in the United States will likely be pivotal for the country's energy security and industrial competitiveness in the green technology market. Continuous updates and situation monitoring are essential as the landscape evolves with discoveries, projects, and policies. Consider checking with relevant governmental agencies and

industry sources for the most accurate and current information. As the lithium demand surges, diverse resource extraction methods are being researched and optimized. This summary provides an overview of significant methodologies, from traditional to innovative, covering extraction from minerals, ores, and seawater. The field is rapidly evolving, with ongoing studies aiming to improve efficiency, sustainability, and cost-effectiveness in lithium extraction and processing technologies. Each method presents its challenges, advantages, and applications, emphasizing the need for continuous research and development in this crucial area.

3.2 Next Steps

Firstly, there should be a diversification of resource exploration efforts. The US needs to undertake exhaustive surveys to discover and evaluate all types of lithium deposits, focusing on regions previously underexplored or unexplored. Support should be provided for geological surveys and exploration initiatives aimed at unearthing lithium resources.

Intensified research is pivotal. Investment in research to develop and optimize various extraction methods for diverse lithium resources is fundamental. The research should not only enhance the efficiency but also improve the environmental sustainability and cost-effectiveness of the extraction processes. Such research should encompass all lithium resources, including lithium brines, spodumene, lepidolite, petalite, and mica.

There's a call for the development of advanced lithium extraction technologies. Notably, existing literature has reviewed and documented various lithium recovery processes, providing a foundation for inspiration and exploration of novel, sustainable lithium recovery technologies from minerals, brines, and Lithium-Ion Batteries (LIBs). The extraction of lithium from minerals and brines is complicated due to the close resemblance in lithium's chemical and physical properties and the associated gangue minerals. Consequently, advanced extraction methods are needed to improve the separation of lithium-bearing minerals from mixtures and rocks. The complexities of efficiently processing spodumene, for example, are highlighted by the impact of various minerals on lithium recovery.

Future efforts should refine electrochemical technologies by enhancing lithium selectivity, material stability, energy efficiency, and cost reduction. Integrating recent technologies is necessary for a successful and sustainable extraction process for lithium-bearing brines. There is also a need to explore Direct Lithium Extraction (DLE) technologies, hydrometallurgical innovations, electrochemical extraction methods, and bioleaching as potential advanced approaches for lithium extraction.

Recycling existing batteries is another crucial pathway. Promoting lithium-ion battery recycling and second-life use of batteries in energy storage applications is vital for sustaining the lithium supply chain and reducing primary extraction dependency.

Policy support is also crucial, where incentives, research grants, and responsible mining and processing regulations should be established to promote domestic lithium production. Furthermore, forging international partnerships will facilitate the exchange of knowledge, technology, and best practices, providing a stable lithium supply and reducing dependence on single sources.

Environmental responsibility in lithium extraction and processing practices is non-negotiable, emphasizing responsible land reclamation and water management practices. Moreover, continuous market monitoring and demand analysis should align domestic production with market needs.

Achieving lithium independence in the US necessitates a collaborative approach involving the government, industry, and research institutions, all committed to innovating in lithium extraction technologies, minimizing environmental impact, and fostering economic growth in the clean energy sector.

4. Possible FY24 scope

4.1 In-depth economic analysis

PNNL has economists, supply chain experts, material scientists, and battery experts to conduct an economic analysis of lithium extraction methods due to the growing significance of lithium as a strategic resource in driving sustainable energy solutions and advancing the United States energy independence and security goals. As a prominent research institution, PNNL is perfectly poised to undertake this crucial task, providing invaluable insights and recommendations that can guide industry practices and government policies. The economic analysis will help optimize the cost-effectiveness and efficiency of lithium extraction processes and ensure that these processes align with environmental conservation and sustainability principles. By undertaking this analysis, PNNL can facilitate the development of a robust, resilient, and sustainable lithium industry, significantly contributing to the nation's transition to a cleaner and more sustainable energy future.

4.2 Determine controlling factors for elevated lithium concentrations

Determining the controlling factors for elevated lithium concentrations through geospatial analysis is pivotal for optimizing extraction strategies and managing the environmental impacts of lithium mining activities. Geospatial analysis allows researchers and industry professionals to identify and understand lithium concentrations' spatial distribution and variability within a geographical area. Recognizing areas with high lithium concentrations is essential for locating economically viable extraction sites, which can significantly influence the feasibility and profitability of mining projects. Moreover, understanding the controlling factors, such as geological formations, mineral compositions, hydrogeological conditions, and available transportation and labor infrastructure, helps develop efficient and environmentally sensitive extraction methods. This understanding is crucial for minimizing lithium extraction processes' ecological footprint and negative environmental repercussions.

4.3 Write an editorial publication

Using this report and the other recommended FY24 scope items to produce a short editorial on lithium in the US would be advantageous for multiple reasons. 1) Public Awareness &

Education: A short editorial can serve as an essential tool for raising public awareness and educating readers about the importance of lithium in the modern economy, its applications, and the implications of its extraction and use. 2) Stimulating Interest: An engaging editorial can stimulate interest among policymakers, investors, educators, and the general public, potentially driving more support and investment into the lithium industry and research initiatives related to it. 3) Shaping Public Opinion: Editorials can help shape public opinion by presenting facts and viewpoints that readers might not have considered, thus fostering a more informed and nuanced public dialogue around lithium extraction, usage, and policies. 4) Highlighting Economic Opportunities: The editorial can spotlight the economic opportunities and jobs the lithium industry provides or could provide in the future, making a case for its significance in the nation's economic landscape. 5) Addressing Environmental Concerns: Through an editorial, concerns regarding the environmental impact of lithium extraction and processing can be conveyed, and potential sustainable practices and innovations in the industry can be promoted. 6) Platform for Experts: It provides a platform for experts and industry professionals to share insights, knowledge, and perspectives on lithium, thereby contributing to the broader discourse on energy, technology, and sustainability. 6) Quick Dissemination: Short editorials are easily accessible and shareable, facilitating quick dissemination of information and ideas among a broad audience. 7) Policy Influence: If the editorial gains traction, it can influence or inform policy and decision-making at various levels of government and within the private sector, potentially leading to more supportive measures for sustainable lithium practices. 8) Public Engagement: Lastly, an editorial can catalyze public engagement and discussion, allowing diverse voices and opinions to be heard and considered.

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Additional papers with valuable insights into lithium concentrations, deposit types, and their significance in global lithium supply.

1. "Global lithium resources: Relative importance of pegmatite, brine, and other deposits" by Meinert et al. (2013) - This article provides an overview of lithium resources worldwide, discussing the relative importance of different deposit types such as pegmatites and brines.

2. "Lithium resources and production: Critical assessment and global projections" by Evans et al. (2013) - This article examines global lithium resources, production trends, and projections for future demand, highlighting the importance of lithium in the context of emerging technologies.

3. "Lithium deposits: Pegmatite, brine, and sedimentary" by Simmons et al. (2016) - This article provides an overview of lithium deposits, focusing on pegmatite, brine, and sedimentary deposits. It discusses their geological characteristics, exploration methods, and production processes.

4. "Lithium deposit geology and resources of the PAK deposit, Guyana" by Chalapathi Rao et al. (2016) - This article focuses on the PAK lithium deposit in Guyana, describing its geological characteristics, mineralogy, and resource estimation.

5. "Lithium resources in the Jadar Basin, Serbia: Geological, mineralogical, and geochemical constraints" by Simic et al. (2019) - This article examines the lithium resources in the Jadar Basin in Serbia, discussing their geological and geochemical characteristics, as well as the potential for lithium extraction.

6. "Assessment of lithium resources and their potential impacts on global lithium markets" by Patterson and Helgeson (2020) - This article assesses global lithium resources, including an analysis of geological, economic, and environmental factors that may influence future lithium production and markets.

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