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Sustainable lithium recovery from hot springs: A multidisciplinary approach

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ABSTRACT

As technology and development advance, global demand for lithium is expected to grow exponentially yearly, hence the need to explore new natural resources to supply the rapid demand. As a leading water resource, lithium is extracted from brines, including salt lakes, geothermal, and oilfield brines. Addressing the lack of studies on new exploitable water resources for lithium extraction, this review presents hot springs as a novel secondary resource for lithium by exploring geological and engineering aspects. The geological section provides information on the genesis of hot springs, mineral structures containing lithium, and the main mechanisms of lithium enrichment in water resources related to water-rock interactions. On the other hand, traditional (i.e., evaporation and chemical precipitation) and advanced lithium extraction engineering techniques, such as direct lithium extraction techniques (e.g., ion exchange, adsorption, solvent extraction, and membrane-based techniques), are here proposed and investigated for hot springs. The review outlines the mechanisms, parameters, and efficiencies associated with the various extraction techniques, highlighting their negative environmental impact and sustainability aspects. Finally, critical aspects and future perspectives are discussed here.

1. Introduction

Lithium, known as 'white gold' or 'white petroleum', is an alkali metal with great energy potential, which is becoming increasingly used in many industrial and economic sectors, including aerospace, ceramics, nuclear, pharmaceutics, metallurgy, glass manufacturing, renewable resources, and high-tech, mainly for energy and storage applications [1,2]. For instance, the electricity sector is one of the current market leaders in terms of lithium demand for the creation of Li-ion batteries (8 kg of lithium are required to produce 60 kWh) for electric vehicles, realizing an energy transition from fossil to renewable energy [3].

Globally, lithium demand tripled between 2017 and 2022, with values in 2021 estimated to be approximately 600,000 tons [2,4], demonstrating how the demand is rapidly increasing. As technology and high-tech industries advance, the global demand for lithium is expected to grow annually up to values 56 times higher than current by 2050, whereas lithium consumption is estimated at 0.38 M-tons by 2028 [5,6]. In this scenario, global lithium production is mainly concentrated in Australia, Chile, China, and Argentina at 47, 30, 14.6, and 4.7%, respectively, with 87% of global lithium demand primarily in Asia [7].

Lithium can be found in natural resources on Earth with different concentration ranges divided into brines (e.g., 1000 mg/L), volcanic and sedimentary rocks (i.e., 20–70 ppm), and the ocean (i.e., 0.18 mg/L) [3]. Currently, brines (e.g., salt-lake brines, geothermal brines, oilfield brines) and lithium hard-rock ores are the main resources exploited for lithium extraction worldwide, with Bolivia, Argentina, and Chile as leaders in salt lake brine reserves (i.e., about 72%), while minerals account for approximately 20% [8].

Although there are abundant natural lithium resources, the growing demand for lithium brings the necessity to explore new and sustainable resources that can soon be exploited to supplement conventional lithium resources that are not unlimited. Besides, brines and ores, thermal waters (e.g., hot springs), as a source and resource for lithium extraction, may represent a viable opportunity to satisfy the increased demand for this metal. Hot springs tend to have lower concentrations of lithium (0.1–250 mg/L) than salt-lake brines (i.e., 500–1800 mg/L), hard-rock

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ores [9–11], but offer sustained and renewable water fluxes (i.e., 1.6 × 10^4 $m^{3/d}$ per hot spring), and does not require energy-intensive mining and roasting processes as do the hard-rock products, which environmental and energy impacts are reported to be approximately 9–60 times higher than those of water-based lithium recovery [12], which resulting in an expected cost between 2 and 80 $/kg [13].

Lithium recovery from water resources (e.g., hot springs) involves a range of technologies, including precipitation and evaporation, as traditional methods, and ion sieves, solvent extraction, and membrane-based technologies as new technologies in the direct lithium extraction (DLE) sector [14,15]. Traditional extraction techniques use solar and wind energy to evaporate the water and concentrate the lithium, whereas recovery is performed using chemical compounds that separate lithium from undesired ions. On the other hand, DLE techniques allow for the avoidance of negative aspects related to traditional methods (e.g., water loss, land use, environmental impacts), achieving higher recovery and extraction efficiencies of lithium using engineering methods based on ion exchange, separation with organic solvents, and filtration with membranes.

Several studies (Fig. 1) worldwide have focused on the investigation of hot springs to understand their physical-chemical characteristics and the concentration of chemical elements (e.g., Li^+) (Table 1), as well as the study of conventional lithium sources (e.g., brines and minerals) for lithium recovery and extraction. Fig. 1a shows a bibliometric analysis of the evolution of scientific studies focused on lithium and hot springs from 2010 to 2024 (Scopus database, data accessed on 14th May 2025). Before 2019, the number of documents was less than 25, but with a slight increasing trend. However, from 2022, substantial growth has been observed, with more than 150 documents reached in 2024. The growth of scientific publications in recent years can be explained by the increased demand for lithium in many economic and industrial sectors, to explore new, unconventional, and sustainable resources. A keyword co-occurrence analysis between correlated contents using VOSviewer software was conducted to identify the main thematic areas and topics (Fig. 1b) using “hot spring” AND “lithium” as keywords in the Scopus database. The generated map (Fig. 1b) is based on the strength of association method by establishing five groups with different themes in geology and engineering, demonstrating the link between the keywords. Lithium and hot springs have the highest association, followed by geothermal fields, hydrochemistry, thermal waters, and groundwater, which are topics of interest in the following review. The network (Fig. 1b) highlights the evolution of research focus from early geochemical characterization and isotopic studies of geothermal systems towards applied research addressing lithium occurrence, hydrochemistry, and extraction-related challenges. Recent clusters have highlighted technical bottlenecks, including low lithium concentration, high temperatures, and complex water chemistry, as well as emerging solutions such as adsorption, membrane-based separation, and resource recovery from geothermal fluids.

To the best of the authors' knowledge, this is the first review focused on hot springs as a possible secondary unconventional source for lithium extraction and possible recovery techniques. Lately, previous review articles have only focused on lithium extraction from salt-lake, geothermal, oilfield brines, lithium-containing wastewater, and seawater, providing information on traditional and advanced engineering techniques in the DLE sector [15–19].

However, none of the above-mentioned review articles focused on the lithium extraction from hot springs using traditional evaporation and DLE techniques, while also providing information on geological aspects correlated to hot springs. To this aim, the specific objectives of this review article was to: *i)* explore geological aspects (e.g., genesis of hot springs, lithium in rocks, water-rock interactions), *ii)* discuss traditional lithium extraction and DLE techniques (e.g., evaporation ponds and chemical precipitation, ion-exchange, adsorption, solvent extraction, membrane-based applications), *iii)* provide critical discussion and future recommendations.

2. Geological overview

Springs are points on the Earth's surface where geothermal waters from underground are discharged. Springs are very different and have been classified in numerous ways based on various parameters such as geology, hydrology, water chemistry, water temperature, and ecology parameters [20]. A hot spring is defined as a source of hot water of deep origin, bubbling out at temperatures of up to 100 °C and related to hydrothermal activity that results from the interaction between a heat source, permeable paths, and circulating fluids [21]. The process of the formation of a hot spring at the surface follows precise steps: (i) water from precipitation infiltrates in the mountainous areas and enters the groundwater system in the form of recharge, (ii) then the water moves into the deep circulation system underground and heating up in contact with the heat of deep sources, (iii) receiving geochemical elements through water-rock interactions and transforming into geothermal water [22]. Hot regions in the depths, represented by active or recently solidified but still hot magmatic reservoirs, allow the water to heat up, which, becoming less dense, rises to the earth's surface via faults, fractures, or fissures [23], leading to the formation of the hot spring. The heat transfer varies depending on the geological system. Thus, the heat is not always directly related to magmatic sources. Moeck [24]divides the sources of transferred heat into convective-dominated and conductive-dominated systems. Convective systems include active volcanic zones, subduction zones and metamorphic complexes as principal systems. In contrast, the main conductive systems include intracontinental fracture basins (host rock: high-low permeability sediments) and intracontinental intrusions in flat terrain (host rock: hot, dry rock). The convective phenomenon is related to the rising of hot magma (molten rock) in the crust and mantle that accumulates in magma chambers, which transfer heat to the surrounding rocks, allowing the water in the rock to heat up and rise [25]. In the conduction phenomenon, heat is transferred through the molecular vibrations of the material in the rock that hosts the fluid. Furthermore, the phenomenon is related to the temperature gradient in the crust that increases with depth [25], with hot dry rocks that transfer heat to the deep water. The two heat transfer systems can coexist. For instance, rainwater once infiltrated at depth and heated by convection from the deep regions rises to the surface. The rise may be hindered by low-permeability surface layers forming vapor condensation at the bottom of the layer: heat here is transferred to the layer through conductive phenomena [26,27].

The origin of a hot spring can occur in different systems, typically distinguished into volcanic hot springs and non-volcanic hot springs: i) volcanic hot springs: these hot springs generally originate near modern active volcanic areas (Fig. 2a), in inactive volcanic zones (Fig. 2b) or in areas where magmatic chambers are present at depth without surface magmatic phenomena (Fig. 2b) [22]. Active volcanic zones are often linked to seismic activities that generate faults and fractures in rocks that become the main pathways for the circulation of subsurface fluids [28] and underground fluids, leading to discharge from aquifers with sufficiently high pressure [29]. Faults and fractures are also the expression of ancient volcanic activity. In active volcanic systems, meteoric water penetrates faults and fractures, reaching deep into magmatic heat sources that heat these waters, allowing them to rise to the surface. For instance, a series of hot springs located near the Changbaishan volcano in Asia originates from continuous heat and degassing of magma coming from multiple magma chambers situated below the volcano in a 5–40 km range and from active faults in the area [30]. Iwamori et al. [31] studied the caldera of the Aso volcano in Japan to understand the circulation of underground fluids, reporting the presence of hot springs around the caldera formed by infiltrating meteoric water and heated by the heat source from the active Aso volcano. The hydrothermal system of the Meakandake volcano is investigated by Takahashi et al. [32]. Dacite magma at depth and magmatic gases at high temperatures (300–600 °C) allow seepage water and shallow aquifers to heat up, forming hot springs and pools on the

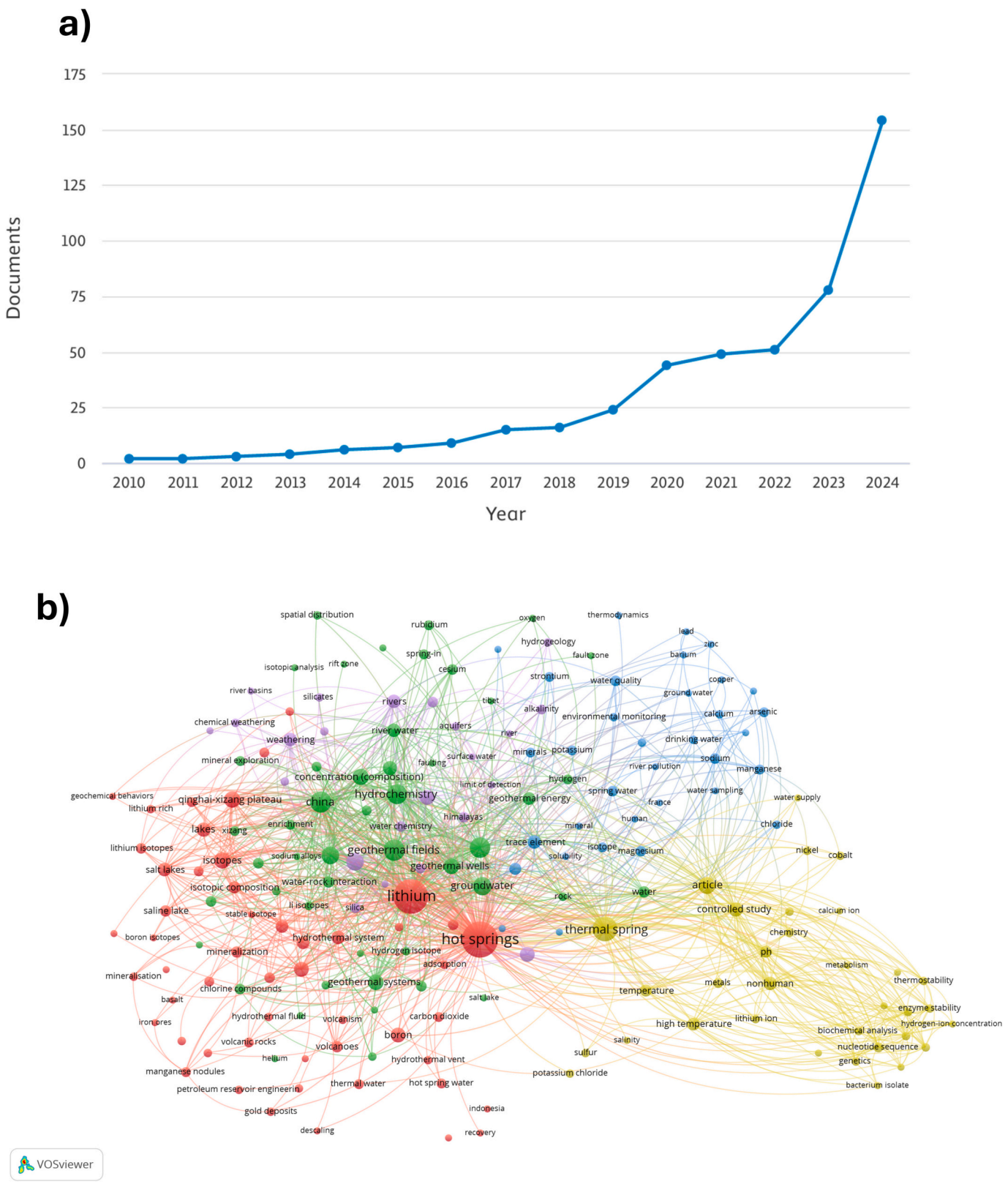


Fig. 1. Investigation of studies related to hot springs. (a) Documents by years (from 2010 to 2024, data accessed on 14th May 2025) and (b) semiquantitative assessment by VosViewer (i.e., co-occurrence) using "hot spring" AND "lithium" as keywords. The thickness of the lines indicates the correlation between keywords. The colors of the lines are determined by the colors of the keywords. The similarity in colors of the keywords reflects their correlation.

Table 1
Overview of Li^+-containing springs in the world (springs with the highest Li^+ concentration are reported for each study).

Springs	T (°C)	pH	Li^+ (mg/L)	Hydrochemistry class	References
Gudui geothermal field, China	53	6.7	34.51	Na-Cl-HCO_3	[76]
Puga geothermal area, India	70	7.8	4.2	Na-Cl-HCO_3	[228]
Strymon Valley, Bulgaria and Greece	60	6.6	1.20	Na-HCO_3	[229]
Zagros Fold and Thrust Belt, Iran	–	6.6	19.4	Na-Cl	[230]
El-Tarf geothermal aquifer, Algerian-Tunisian border	67	6.2	0.742	HCO_3–Cl–Na–Ca	[231]
Terme Ciorra Spring, Suio Thermal Field, Italy	47	6.4	1.1	Na–HCO_3–SO_4	[10]
Nagano, Japan	16.6	7.9	62.2	–	[232]
Xianhaizi Geothermal Spring, Tibet	60–70	7–8.5	239	Na-HCO_3	[9]
Semi-Dazi Geothermal Field, Tibet	–	6.5–8.5	35.6	Na–HCO_3–Cl	[233]
Way Ratai Geothermal Springs, Indonesia	89	7	8.11	Na-Cl	[112]
Pagosa Hot Springs, Colorado, USA	62	6.6	2.9	Na-SO_4-Cl	[234]
Jonzac, France	–	8	3.5	Na–Cl–SO_4	[235]
Sarturnia Thermal Springs, Italy	37.5	6.4	0.19	Ca–Mg–SO_4	[236]
Xiong'an New Area, China	75–95	6.5–7.5	1.388	Na–Cl–HCO_3	[237]

surface, while fractures in the rock allow hot gases to rise with fumaroles forming in the crater zone. The genesis of hot springs can also involve inactive volcanic systems, as expressed by Liu et al. [33] in their research on the geothermal area of the Tatun Volcano Group in Asia. The volcanoes in this system are considered dormant or extinct, and the residual magmatic chamber at depth serves as a heat resource for forming fumaroles, solfataras and hot springs at the surface.

ii) Non-volcanic hot springs: hot dry rocks at depth interact with groundwater to create hot flows that rise to the surface to form hot springs (Fig. 2c). Hot dry rock is a rock mass with no or only a few fluids inside, temperatures higher than 180 °C and thermal energy [34]. Hot dry rocks usually include metamorphic rocks (e.g., gneiss, quartzite, schist) and intrusive rocks (e.g., hard granite). Leng et al. [35] conducted a systematic study of the Hainan Island area in China, demonstrating the presence of heat reservoirs associated with granitic rocks at a temperature of 236 °C and a depth of 6000 m, responsible for geothermal activity expressed in the form of surface hot springs. Furthermore, Bandara et al. [36] proposed a series of heat resources, including magmatic intrusions, radioactive ore deposits, and an elevated geothermal gradient, to explain Sri Lanka's foreland hot springs, which originate from infiltrated rainwater and are dominated by fault systems. Sedimentary environments, such as sedimentary basins, can also host hot springs due to interactions between infiltrated rainwater and the deep rocky heat source, as expressed by Saibi [37] and Adams [38]. The water in the pores of the sedimentary rocks is heated by conductive heat flow from below [37]. In some situations, hot springs are formed through the interaction between carbonate structures, which act as fractured reservoir rocks (aquifers), and a hot resource at depth (Fig. 2d) [39]. For instance, Saroli et al. [40] proposed and studied an underground hydrogeological model to understand the presence of hot springs in Suio Terme, Italy. Hot springs are formed through water derived from the carbonate hydrostructure, which, in contact with heat from metamorphic rocks at depth (heat coming from peri-Tyrrhenian volcanism), is warmed and pushed to the surface through faults, mixing with cold water from the carbonate complex and assuming temperatures of up to 50 °C.

Generally, water heated at depth during ascension tends to cool gradually, assuming lower temperatures at the surface than in the deeper bands. Temperature, as mentioned previously, is used as a parameter to classify springs; we distinguish cold springs (<20 °C), warm springs (20–30/40 °C) and hot springs (> 50 °C).

2.1. Lithium in rocks

To understand how lithium ion (Li^+) is present in hot springs and other liquid sources and to learn about the mechanisms that allow Li^+ to be present in them, it is necessary to start with the rocks and minerals that contain lithium. Lithium resources in natural rocks are mainly stored in igneous and sedimentary rocks [12]. Among igneous rocks, granite and pegmatites are the most widespread, with the most important lithium minerals such as spodumene ($LiAlSi_2O_6$) and petalite ($LiAlSi_4O_{10}$) [41]. The process of pegmatite formation begins with molten magma, continuing through the cooling and crystallization of granitic magma with possible interactions with hydrothermal conditions at the end of the formation [42]. During fractional crystallization of the magma for granite formation, the typical minerals that crystallize first are alkali feldspar, sodic plagioclase, quartz, and smaller amounts of muscovite or biotite. At the same time, volatiles (e.g., H_2O, B, F) and elements incompatible with the crystalline structure of the common crystals (e.g., Li, Cs, Ta) remain in the residual magma liquid [43]. Subsequently, the residual liquid enriched in elements penetrates fractures in the crust, solidifying and giving rise to pegmatites and lithium-based minerals. Volatiles enhance elements' mobility, reduce the liquid's temperature and viscosity, and promote the formation of large crystals [44]. The formation of pegmatites by fractional crystallization of granitic magma is widely accepted as a formation model [45]. Nonetheless, direct formation via anatexis and liquid immiscibility seems to be another possible formation model for pegmatitic rocks [43,46]. Lithium minerals are often intensely altered during the post-magmatic phase of pegmatite development through interaction with hydrothermal fluids that leach Li from the late stage of pegmatite crystallization into these fluids [47]. However, Li mineralization in pegmatites depends on the Li contents in ore-forming melt, and the crystallization of Li-bearing minerals requires a lithium oxide (Li_2O) content of 1.5–2.0 wt % [48], whereas Li-rich pegmatites require a temperature between 400 and 600 °C and a pressure of 5 to <2 kbar [49]. Interactions between fluids derived from pegmatites during crystallization and adjacent host rocks can form Li enrichment in rocks different from pegmatites. Keyser et al. [50] show that pegmatites studied in Austrian deposits have a lithium enrichment of >1.5 wt% Li_2O. In contrast, contact between pegmatite fluids and adjacent metamorphic rocks (schists and amphibolites) resulted in Li enrichment in host rocks with concentration values above 590 and 390 ppm, respectively.

Spodumene, as mentioned previously, is the most important lithium mineral found in pegmatites, with an ideal composition of ~8.03 wt% Li_2O and a monoclinic crystal structure with Si in the tetrahedral coordination, Al in the M_1 crystallographic site and Li in the M_2 crystallographic site [49]. Petalite also has an ordered monoclinic structure with

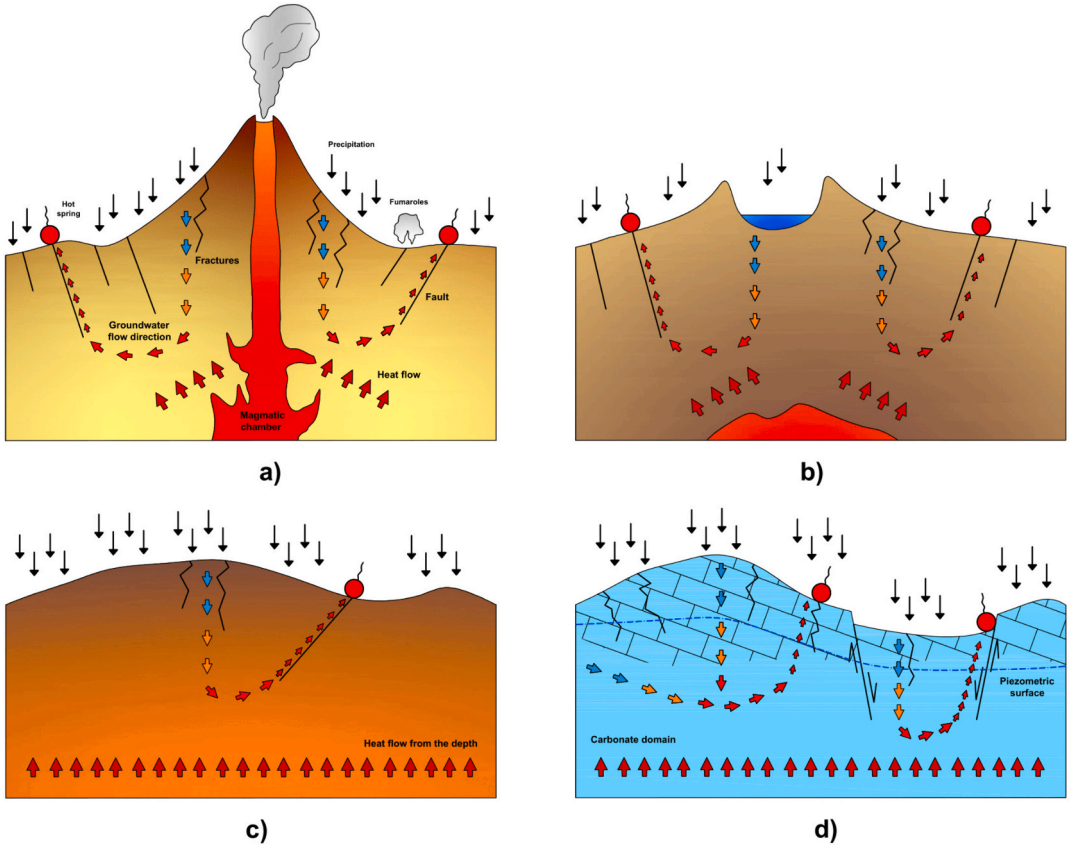


Fig. 2. Schematic profiles of hot spring formation. (a) Hot springs formed in an active volcanic zone. (b) Hot springs formed in a non-active volcanic zone in the presence of a residual magma chamber. Hot springs in a non-active volcanic zone with a crater lake. (c) Hot springs in a non-volcanic zone formed by the interaction of infiltrated water with heat from hot crustal rocks at depth. (d) Hot springs formed in a faulted and fractured carbonate domain.

the silicon tetrahedra and aluminum octahedra in layers and the Li atoms in interstitial spaces, with a theoretical Li_2O content of ~4.50 wt % [51]. Besides these primary minerals, literature also indicates other Li-related secondary minerals, including lepidolite, amblygonite, zinnwaldite, triphylite, and eucryptite [52,53]. Generally, spodumene in pegmatites is also often associated with mica, quartz, and feldspars. For instance, pegmatites with albite-spodumene minerals are lithium-rich mineralized pegmatites characterized by the presence of quartz, albite, and spodumene compared to k-feldspars, and with the bulk pegmatite Li concentration around 2 wt% Li_2O [54]. Indeed, albite is a common feldspar found in pegmatites that crystallizes over extensive solidification periods and serves as a suitable host for Li and other elements such as Cs, Rb, Sr, Pb in the alkali position [43]. Ties of this type are also detected by Sha et al. [55] in the Kelumute-Jideke pegmatite field with 65,000 tons of proven Li_2O resources and a quartz-albite-spodumene primary ore assemblage in >70 vol%. Breasley et al. [56] reported the study of the pegmatite deposit of Tanco, Canada, where Li mineralization occurs mainly as a spodumene-quartz assemblage from petalite breakdown as the primary mineral formed during melt crystallization.

In the sedimentary world, lithium is predominantly stored in the ores of clay sedimentary deposits [57]. Li is primarily present in the mineral smectite in clay-based sedimentary deposits, with the most common expression of Li-rich hectorite [41]. However, sedimentary clay deposits are divided into three categories: (i) hectorite-type deposits, (ii) mixed illite-smectite deposits and (iii) Jadarite type. Smectite and illite possess a 2:1 layered structure with two tetrahedral sheets and one octahedral sheet [58]. In contrast, jadarite, a new mineral discovered in Serbia deposits, presents a layer of corner-sharing, tetrahedrally coordinated Li, Si, and B forming an unbranched single layer, which is decorated with triangular BO_3 groups, Na between the tetrahedral layers, and H located on the apex of the triangular BO_3 group [59]. The concentration of Li in these sedimentary minerals depends on the mineralogical and diagenetic characteristics of the rock formation site. Generally, the concentration of Li in illitic clays ranges from 3000 to 6000 ppm, whereas in illitic-smectitic clays it ranges from 2000 to 3000 ppm [57]. On the other hand, the Li content in jadarite is estimated to be 7.2–7.3 Li_2O wt% [60].

Other classifications suggest a subdivision of clay-Li mineral resources based on origin into volcanic and non-volcanic (sedimentary, lacustrine) types [61,62]. Volcanic clay-Li minerals deposits originate from the leaching of lithium present in volcanic ash and rhyolitic and dacitic lavas by meteoric and hydrothermal fluids, and successively enriched in clay minerals (e.g., hectorite, smectite), forming sediment Li deposits in caldera basins [63,64]. A volcanic-sedimentary model may originate when lithium-rich volcanic deposits are altered in closed sedimentary environments and reworked as sediments with the subsequent formation of lithium clays. For instance, Castor and Henry [65] illustrated in their study the formation process of the Li-rich clay deposit (illite and smectite, Li content ~2000 ppm) of McDermitt, USA, through closed hydrological system diagenesis of the tuffaceous host sediments in the closed caldera basin. Lin et al. [66] studied the Li-rich illite deposits of Xiejiacao, South China, showing the bond between volcanic material deposited in the marine basin and post-sedimentary alteration, forming clay minerals. Furthermore, the Jadar deposit in Serbia is another example of a volcanic-sedimentary model of a Li deposit as suggested by Putzolu et al. [67]. In non-volcanic models, Li-clay minerals are formed by weathering of lithium-containing parent rocks with subsequent transport of Li into evaporitic lacustrine basins and formation of lithium minerals through interaction with soil and basin sediments [68–70]. Adsorption and ion-exchange are the main mechanisms

of Li-clay ore formation, with Li being incorporated into the crystal lattice of the minerals. Lacustrine sediments based on Li-clay minerals in Clayton Valley, NV, are an example of Li enrichment in a closed sedimentary basin with a Li content in the bulk sediments up to 1700 ppm [71]. Also, a model of carbonate-hosted clay-type Li resources is proposed by Wen et al. [72] associated with carbonate weathering-sedimentation mechanisms, not related to volcanism or hydrothermal fluids and in environments such as coastal marshes, lagoons and limited and closed basins that are ideal for Li enrichment and formation of large deposits. In these systems, Li is mainly stored in minerals such as montmorillonite and chloride [68,72]. Several recent studies have reported the presence of significant carbonate-hosted clay-type Li resources in South-West China with Li contents around 1000 ppm or higher and related to the presence of illite, montmorillonite and chlorite as major host minerals [73,74].

2.2. Water-rock interactions and hydrochemistry of hot springs

Fluid-rock interaction is a chemical natural process where a fluid and a rock in thermodynamic disequilibrium come into contact by realizing chemical exchanges to reach equilibrium [75]. During the upward migration, groundwater undergoes various hydrochemical processes with the host rocks, including leaching, hydrolysis, and ion exchange [76]. However, this process occurs under hydrothermal conditions of high temperature and pressure, and both rock and fluid become hydrothermally altered with a chemical composition different from the original. Referring to lithium, it is well established that hot waters (e.g., hot springs) enriched in Li^+ are associated with deep leaching of host rocks and water-rock interactions as one of the primary methods of Li^+ enrichment [76–78]. The transition of lithium from the rock to the liquid phase and subsequent enrichment occurs due to the high mobility and solubility of Li^+ compared to other cations [79,80] and temperature binding, with Li^+ concentration increasing with higher temperature [9,81]. Moreover, high-viscosity liquids and low-permeability host rocks may hinder fluid-rock interactions, decreasing the solid-liquid contact surface area and limiting ion exchange [75].

2.2.1. Water-rock interactions: Altered lithium minerals

Contact between lithium minerals in the rock and hot fluids leads to a series of chemical reactions, resulting in lithium leaching and ore alteration. Spodumene, as the main lithium-based mineral, tends to decompose quickly under hydrothermal conditions, becoming an altered ore with water in its microstructure (e.g., OH^-) and a lower Li content due to leaching [82]. During decomposition of the crystal lattice by acidic fluids in the late-final stages of hydrothermalism, Li is released into solution and spodumene is replaced by secondary minerals such as cookeite, muscovite, albite, quartz and k-feldspars [83,84], becoming altered. For instance, Bobos et al. [85] reported the reaction of the formation of cookeite and quartz from spodumene (Eq. (1)), whereas Yin et al. [83] showed the reaction of the formation of muscovite and quartz from spodumene (Eq. (2)).

$$5LiAlSi_2O_6 + 4H^+ + 2H_2O \rightarrow LiAl_5Si_3O_{10}(OH)_8 + 4Li^+ + 7SiO_2 \quad (1)$$

$$3LiAlSi_2O_6 + K^+ + 2H^+ \rightarrow KAl_3Si_3O_{10}(OH)_2 + 3SiO_2 + 3Li^+ \quad (2)$$

The deterioration of the ore structure in contact with highly acidic fluids is the main factor in the high reactivity of the mineral with an increased extraction of cations from the original structure (e.g., Al, Li) [86]. Chen et al. [87] described spodumene and muscovite alteration in pegmatites of the Altai orogenic belt, North-West China, demonstrating how late hydrothermal fluids leach Li from primary minerals and how enrichment occurs in the fluid phase. Studies on the coal seam of Jincheng Coalfield, North China, conducted by Zhang et al. [88] suggested that the carrier of Li in the Li-rich No. 3 coal is associated with the presence of cookeite formed by hydrothermal fluid activity related to intrusive magmatic activity.

As illustrated previously, in the first stage of hydrothermal alteration, the spodumene is replaced by secondary minerals (mainly cookeite), nonetheless, a continuous contact with hydrothermal late-stage acidic fluids results in an advanced argillization process with the formation of clay minerals such as kaolinite, muscovite and illite in this secondary stage of alteration [82]. The secondary mineral cookeite is altered to muscovite/illite, and kaolinite is formed. The presence of K^+ in the acid fluid and medium-high temperatures facilitates the formation of muscovite and illite. In contrast, the absence of K^+ during hydrothermal processes promotes kaolinite's direct formation from cookeite.

Wang et al. [89] recommended that the high concentration of Li in the thermally altered coal of Fengfeng coalfield, China, is stored in the cookeite and in the clay minerals layered structure by heat derived from thermal activity. On the other hand, recent studies indicated how cookeite formation is possible also through a hydrothermal alteration of a pre-existing Li-enriched clay minerals [54,61] and how cookeite, as a secondary mineral, can be further leached by acidic fluids to allow Li migration within the liquid phase [90]. Indeed, in the secondary stage, the formation of clay minerals causes the leaching of Li from cookeite, as evidenced by the following simplified reaction describing the alteration of cookeite to muscovite (Eq. (3)):

$$LiAl_5Si_3O_{10}(OH)_8 + K^+ + 6H^+ \rightarrow KAl_3Si_3O_{10}(OH)_2 + Li^+ + 2Al^{3+} + 6H_2O \quad (3)$$

Petalite, as a primary phase mineral, can also be altered during the late stage of evolution of granitic pegmatites by residual fluids and replaced by other minerals such as albite, K-feldspar, mica, and clay minerals [91]. Acid fluids, rich in H^+, quickly attack the structure of petalite, allowing Li to pass through the liquid phase and form replacement minerals such as mica and clay minerals. Whereas alkaline fluids, rich in Na^+ and K^+, facilitate the formation of albite and k-feldspar and the release of Li into the fluid as expressed by the simplified exchange reactions (Eq. (4), Eq. (5)) [92]:

$$LiAlSi_4O_{10} + Na^+ \rightarrow NaAlSi_3O_8 + SiO_2 + Li^+ \quad (4)$$

$$LiAlSi_4O_{10} + K^+ \rightarrow KAlSi_3O_8 + SiO_2 + Li^+ \quad (5)$$

A multidisciplinary study is conducted by Cardoso-Fernandes et al. [93] to understand the alteration products of petalite from Bajoca pegmatites, Portugal: the results show two stages of alteration, one under acidic conditions with kaolinite formation and one under alkaline conditions with illite-montmorillonite formation. Reflectance spectroscopy, microscopy and geochemical studies were carried out by Cardoso-Fernandes et al. [94] on samples of Fregeneda-Almendra pegmatites (Spain-Portugal), identifying petalite alteration products, mainly illite and montmorillonite, followed by kaolinite and saponite (Mg-smectite).

Lithium-rich clay minerals, such as hectorite and smectite, often form through hydrothermal alteration processes, where silicate rocks interact extensively with thermal waters enriched in alkali metals. During these reactions, lithium is preferentially leached from primary silicate minerals and subsequently incorporated into secondary clay minerals or released directly into geothermal fluids, depending on environmental conditions such as temperature, pressure, pH, and fluid chemistry [95]. The transition of lithium from rock to fluid is mainly governed by hydrolysis reactions that break down primary minerals like spodumene, petalite, and lepidolite, leading to the release of Li^+, which are stabilized within the fluid phase or reprecipitated as secondary Li-bearing minerals [79]. Globally, this alteration process has been documented in several notable geothermal systems, including the Clayton Valley (Nevada, USA), the Salton Sea (California, USA), and the geothermal fields of the Taupo Volcanic Zone (New Zealand), each representing key examples of active lithium enrichment and extraction potential [96,97]. Understanding these alteration mechanisms provides valuable insights for optimizing lithium recovery from thermal springs

and identifying promising geothermal resources worldwide.

2.2.2. Hydrochemistry of the hot and thermal springs

The hydrochemical characteristics of hot springs reflect complex interactions between meteoric waters, deep geothermal fluids, and the geological environment, offering key insights into the dynamics of the geothermal systems. An analysis of the hydrochemical characteristics of these waters is essential to understand their origin, circulation paths, and the type of water-rock interactions. The concentration of different dissolved ions, in fact, allows for assigning a specific category and classification to each water.

Hydrochemical classification of thermal springs, broadening the discussion to all geothermally heated waters, is frequently based on major anions (Cl^-, SO_4^{2-}, HCO_3^-) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) concentrations, typically visualized using ternary diagrams such as the Cl–SO_4–HCO_3 and Na–K–Mg diagrams, which effectively highlight the dominant geochemical processes controlling water chemistry [98]. The concentration of dissolved ions in thermal spring waters is controlled by multiple factors, including: (i) temperature and pressure, which enhance mineral solubility; (ii) residence time, which increases the extent of water-rock interaction and ion enrichment; (iii) the type of host rock, whose mineralogy dictates the specific ions released; and (iv) mixing processes with surface waters or other aquifers, which can dilute or modify the original hydrochemical signature.

In general, the chemical composition of thermal waters varies significantly according to the geological framework, including interactions with different rock types, tectonic settings, and the presence of volcanic activities [99–101]. For example, thermal springs located near carbonate rocks typically show elevated bicarbonate (HCO^{3-}) concentrations, reflecting intense water-carbonate rock interactions, while those in volcanic regions often display increased chloride (Cl^-) and sulfate (SO_4^{2-}) concentrations due to deep-seated magmatic gas interactions [32,101]. Thermal springs of the northern Sichuan-Yunnan block, situated in active fault zones, predominantly exhibit Na-HCO_3 and Na-HCO_3-Cl water types, suggesting deep circulation paths and interactions with crustal and mantle-derived gases [102]. In other regions, such as the Taupo Volcanic Zone in New Zealand, thermal waters are commonly NaCl-type, directly derived from deep geothermal reservoirs [103]. In contrast, hot springs from the Sichuan Basin, China, show predominantly SO_4-Ca characteristics due to the dissolution of sulfate minerals like gypsum and anhydrite in aquifers hosted in sedimentary basins [104].

Several studies illustrate the use of ternary diagrams and isotopic analyses to classify thermal waters and understand their origins. These include comprehensive investigations in geothermal fields such as the Ulleungdo volcanic island, South Korea [96], the Gudui geothermal field, Qinghai-Xizang Plateau, China [76], and geothermal systems in southern Italy, including the active volcanic island of Ischia, known for vapor-dominated geothermal systems with complex geochemical interactions between meteoric inputs and magmatic fluids [105].

Thermal springs from volcanic and non-volcanic regions can also be distinguished clearly based on their geochemical signatures. For instance, in East Malaysia, volcanic thermal waters exhibit the Cl-HCO_3-SO_4-Na type, while non-volcanic sources predominantly display K-Na-HCO_3 characteristics, reflecting variations in geothermal reservoir temperatures and origins [106]. The hydrothermal areas of Taiwan's Tatun Volcano Group further exemplify the complexity of geothermal waters, classified into distinct types: acidic SO_4^{2-}, neutral HCO^{3-}, and Cl-rich acidic waters, each type reflecting specific volcanic activities and geological structures [33].

In addition to major and minor ions, trace elements, such as Li^+, in thermal waters are increasingly important for their value as geochemical tracers and potential economic and therapeutic interest. Its concentration in thermal waters is closely linked to the geology of the hydrogeological basin and to the water-rock interaction processes that occur at high temperatures. The main sources of Li^+ in thermal waters include the alteration of Li-bearing silicate rocks, particularly felsic igneous and metamorphic lithologies such as granites, pegmatites, and associated clays containing minerals like lepidolite or spodumene, where prolonged interaction with hot fluids promotes lithium dissolution [95,97]. Additionally, ion exchange with clay minerals such as smectites and illites can mobilize or retain lithium depending on temperature and fluid chemistry [107]. In some geothermal systems, lithium is also introduced through deep-seated magmatic fluids or degassing processes [32,108], while contributions from evaporitic rocks, though less common, may supplement the ionic composition [109]. Overall, temperature plays a pivotal role, with higher thermal regimes enhancing mineral solubility and Li enrichment in solution [110].

The occurrence of lithium in thermal waters is geographically widespread. High concentrations of lithium are commonly associated with felsic igneous and metamorphic rocks, particularly in systems where geothermal fluids interact with Li-bearing granites, pegmatites, or leucogranites, as observed in the Gudui geothermal field in Tibet [76]. Other notable examples include the Salton Sea geothermal field in California, where high-temperature brines contain lithium concentrations exceeding 400 mg/L, and the Zabuye Lake system in Tibet, where ancient geothermal processes played a key role in Li enrichment [18,111]. Lithium-rich salt lakes on the Tibetan Plateau provide another example of distinct hydrochemical conditions, strongly influenced by the input of lithium-enriched geothermal waters and weathering of surrounding silicate rocks [108]. These environments share key geochemical features, including elevated temperatures, magmatic degassing, and prolonged water-rock interaction, all of which contribute to the mobilization and enrichment of lithium in geothermal fluids.

At a global scale, lithium concentrations in thermal waters are known to vary widely (Table 1.), but several large-scale studies have demonstrated common enrichment mechanisms and spatial patterns. For example, Li et al. [111] compiled over 300 hydrogeochemical data points from geothermal springs across the Qinghai–Tibet Plateau, revealing that silicate weathering and geothermal input are the primary sources of lithium in these waters. Similarly, Arrofi et al. [112] showed how seawater mixing in the Way Ratai geothermal field (Indonesia) enhances lithium solubility in andesitic systems. Studies from the Himalayan collision zone also confirm lithological control on lithium content in thermal waters, supported by isotopic evidence [113]. Although regional variability is high, these findings underscore the significance of geological structure, magmatic input, and hydrothermal dynamics in controlling lithium availability worldwide.

In Europe, lithium-enriched geothermal fluids have been identified in at least 182 documented occurrences across sedimentary, granitic, and metamorphic rocks. Concentrations of Li range from 15 to 480 mg/L, with higher values consistently associated with Na—Cl brines and elevated contents of K, Rb, B, SO_4, and F, indicators of both high-temperature and high-salinity conditions. These chemical signatures reflect advanced water-rock interaction, particularly with Li-bearing granites and evaporitic rocks subjected to hydrothermal alteration. Furthermore, the strongest lithium enrichments are often linked to regions with a history of crustal extension or post-orogenic tectonic relaxation, such as the Upper Rhine Graben or the Paris Basin. This suggests that both geological framework and fluid chemistry are critical factors in driving lithium mobility and concentration in European geothermal systems [114].

3. Hot springs vs other lithium-based resources

Hot springs, as a lithium-based water resource, are similar, but at the same time, show some differences in chemical composition and other properties (e.g., temperature and salinity) to salt lakes, geothermal and oilfield brines, making them suitable for possible exploitation for Li recovery. Generally, hot springs have temperatures ranging from 10 to 100 °C depending on the area and chemical composition, varying depending on water-rock interactions. Typically, hot springs rich in Na^+

and HCO_3^- are alkaline with pH values greater than 7, while high concentrations of Cl^- and SO_4^{2-} result in acidic conditions with pH values below 7 and close to 5. Ca^{2+}, Mg^{2+}, Na^+, Cl^-, HCO_3^- and SO_4^{2-} are the main elements found, combined with minor trace elements such as Li^+. Salt-lake, geothermal, and oilfield brines follow the same compositions and classifications as hot springs, with a greater predominance of Na^+, Cl^-, Ca^{2+}, and Mg^{2+} ions in salt-lake and geothermal brines, and Na^+ and Cl^- ions in oilfield brines [115,116]. However, oilfield brines also contain hydrocarbons, organic acids, inorganic materials, additives, and various heavy metals derived from gas and oil recovery operations [116,117]. The temperature of oilfield brines varies between 20 and 90 °C depending on the area, while for geothermal brines it ranges between 50 and 350 °C, reaching the highest temperatures at greater depths [117]. The temperature of the salt-lake brines is equal to the ambient temperature or modestly warm. Hot springs have lower salinity than brines, typically up to 20–30 g/L, whereas brines can reach 300–400 g/L [116,118], significantly exceeding the salinity of seawater (e.g., 32–36 g/L) [119]. Considering these features, the Li recovery process currently used for brines can also be applied to hot springs without any major differences, with the aim of maximizing recovery by pre-concentrating and removing interfering substances. Furthermore, compared to other lithium-based resources, such as ore mining, there are fewer negative environmental impacts and less energy consumption and emissions. Ore mining uses acid, alkaline and roasting techniques to extract Li from minerals, resulting in high fossil fuel consumption with associated emissions, electricity and steam during the purification stages, and the formation of mixed waste solutions based on acid chemicals and other pollutants generated during the acidification and calcification processes [12]. From an environmental perspective, extracting Li from mineral sources requires a considerable amount of energy and natural resources, resulting in the release of high quantities of pollutants that impact on the environment approximately 9–60 times that of extracting lithium from water resources (e.g., hot springs and brines) using traditional and new techniques [12,120].

Considering the physical-chemical properties described above, when designing an extraction strategy, attention should be paid to specific aspects that distinguish hot spring systems from other brines. Hot springs exhibit a significantly lower lithium concentration (i.e., 0.1–250 mg/L) and salinity, but a higher amount of Ca^{2+} and Mg^{2+} than salt-lake and geothermal brines. These conditions need a selective separation step to overcome the issue of competitive ions (e.g., high Mg/Li ratio) and an additional pre-concentration step for Li-ion recovery. On the other hand, oilfield brines contain hydrocarbons and other organic compounds, which are not generally included in hot springs, whereas geothermal brines present high temperatures and total dissolved solids. Therefore, although extraction techniques, such as adsorption, ion exchange, solvent extraction, and membranes, are also used for other lithium resources, as in other environmental engineering applications for water purification, but their operating performance, selectivity conditions, and pretreatment requirements are unique for hot springs and are described in the following sections.

4. Traditional lithium extraction

4.1. Evaporation ponds and chemical precipitation

Lithium extraction (i.e., approximately 70% of world reserves) through the evaporation of natural water resources (e.g., thermal springs) is most common in the lithium recovery industry due to its low cost and abundant reserves [121]. For instance, Chile and Bolivia represent the principal lithium producers using brine as a source (e.g., Atacama and Uyuni salt lakes), due to a Li concentration exceeding 1800 and 500 mg/L, respectively, and estimated reserves of over a million tons [122–124].

Hot spring water evaporation can occur in open ponds to maximize the lithium salt concentrations (e.g., lithium chloride (LiCl)) and proceed to a purification and refining phase (Fig. 3). Indeed, the natural Li^+ concentration of thermal springs is low (i.e., approximately 0.1–250 mg/L) [9,10] for a cost-effective extraction without a pre-concentration process. Thus, wind and solar energy allow the thermal spring to evaporate and concentrate Li^+, and subsequently to use the lithium-rich source (e.g., above 1000 mg/L) for a recovery process [125]. The refining process generally involves chemical addition for pH modification, precipitation, filtration, drying, and cooling [126]. Therefore, a plant close to the ponds can be located for LiCl conversion (Fig. 3) into lithium carbonate (Li_2CO_3) (at pH 10.5–11, Eq. (6)) or lithium hydroxide (LiOH) (Eq. (7)) as commercial raw materials to produce other lithium compounds based on the industry target:

$$2LiCl + Na_2CO_3 \rightarrow Li_2CO_3\downarrow + 2NaCl \quad (6)$$

$$Li_2CO_3 + Ca(OH)_2 \rightarrow 2LiOH + CaCO_3\downarrow \quad (7)$$

However, the whole extraction method can cope with some issues, such as climate conditions and ion interferences. In order to guarantee the evaporation conditions of the ponds, an arid climate, low salt water permeability, unidirectional winds, and limited rainfall are required [127]. In addition, since thermal springs are rich in other ion salts such as Ca^{2+}, Mg^{2+}, and SO_4^{2-} [10], the extraction technique would require chemical addition to avoid co-precipitation, further complicating the Li recovery process.

Therefore, $Ca(OH)_2$ (spent lime) can be priorly added during a clariflocculation process (at pH 9–10) to precipitate the Mg^{2+} as magnesium hydroxide ($Mg(OH)_2$), generating calcium sulfate ($CaSO_4$) (Fig. 3). Sodium carbonate (Na_2CO_3) can be subsequently employed to remove the residual Ca^{2+} as calcium carbonate ($CaCO_3$) [125,127] (Fig. 3). The obtained sodium sulphate (Na_2SO_4) can precipitate in the presence of cooling systems after lithium removal (Fig. 3) [128].

On the other hand, Mg^{2+} ions show a similar chemistry compared to Li-ions, which can co-precipitate as carbonate (Li_2CO_3), thus leading to increased costs and decreased LiCl generation. For this reason, the Mg/Li ratio represents a crucial parameter for hot spring-derived brine. High Mg/Li ratios correspond to values >10, whereas low ratios are ≤10 Solutions with a low Mg/Li ratio would represent an economical and sustainable option for lithium extraction using traditional evaporation

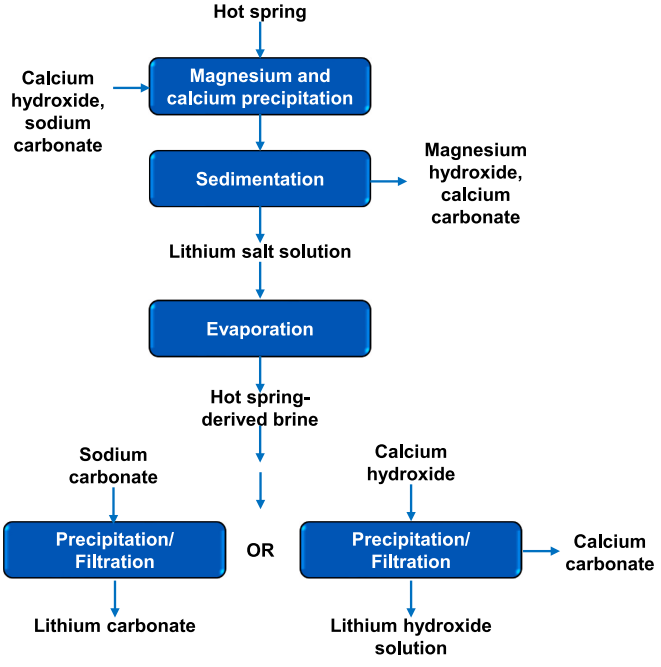


Fig. 3. Lithium recovery from hot spring water by involving evaporation ponds, chemical precipitation and separation/filtration techniques.

and precipitation methods rather than the other classified brine (i.e., high Mg/Li ratio).

4.2. Advantages and disadvantages

The mechanism of evaporating ponds shows some advantages, such as high recovery capacity, final product purity, high efficiency, high yields, cost-effective technology, and simple processes. For instance, an efficiency above 90% and a purity of approximately 99% were achieved from brine by an evaporation process to produce lithium carbonate in the final precipitation at 80–90 °C [129]. A high recovery efficiency (i.e., approximately 99%) was also obtained by Shi et al. [130] with an evaporation process including removing boron, an impurity hindering the lithium chloride production. Ma et al. [131] obtained an efficient enrichment of Li^+ in the resulting brine from about 274 to 36,000 mg/L, utilizing natural energy for the evaporation with a yield of 64%. An enrichment process with solar ponds was shown by Yang et al. [132] with oilfield brine after passing through six different solar ponds, by increasing the lithium concentration from 170 to approximately 9000 mg/L.

Despite the advantages, there are several drawbacks related to the use of evaporitic technologies, i.e., water loss, carbon dioxide emissions, long evaporation time and land usage.

During the evaporation by solar energy, 85–95% of the thermal water can evaporate into the atmosphere, and therefore, only a portion of the water can be effectively returned to the groundwater. Indeed, water loss from evaporation in ponds was estimated to range between 400 and 2 million liters per kilogram of lithium [133]. Also, an elevated amount of fresh water from the surface resources needs to be consumed in plants during the refining activities aimed at producing Li_2CO_3. Water loss is a significant issue, not only due to critical environmental impacts (e.g., desertification, degradation of the surface vegetation), but also to water resource issues towards local communities, especially in arid and semi-arid areas with low annual precipitation.

Lithium enrichment in solar evaporation ponds requires a lot of energy and chemical usage to abate impurities. These two aspects contribute significantly to increasing CO_2 emissions and potential global warming. In the raw brine, the main factor influencing the emissions and environmental impacts is the initial grade of lithium [134]. Indeed, more impurities in the salt solution require more steps, energy, and chemical use to produce lithium compounds such as Li_2CO_3.

The evaporitic process generally takes 12–24 months to reach the desired lithium concentration. Today, prolonged periods and significant cost effects push to abandon traditional extraction techniques in favor of advanced techniques that can get lithium quickly and with maximum efficiency, such as DLE, which have timescales not exceeding 2 weeks [135].

Also, land use can be another critical point, with wellfields, large ponds, and processing plants contributing to high land use with traditional extraction techniques, leading to consequent environmental impacts such as desertification, biodiversity loss, and vegetation death. For instance, Mousavinezhad et al. [134] reported that the land use of approximately 357–659 m^2 per ton of lithium carbonate produced.

Therefore, the sector is trying to move towards advanced extraction techniques to cope with the abovementioned issues, such as using DLE techniques.

5. Direct lithium extraction techniques

DLE is an emerging set of technologies aimed at addressing the limitations of the conventional method of evaporative lithium extraction from hot spring waters. Indeed, Li recovery from hot spring-derived brines is a resource-intensive process in water and reagent consumption (e.g., acids, bases, precipitating reagents), with a production time of up to 2 years [136]. These techniques promise faster extraction times and higher yields, potentially expanding the range of usable hot spring resources across different geographic locations. Among other advantages, the reduction of environmental impacts, low water usage, and high selective extraction are among the various DLEs [135], e.g., ion exchange, adsorption, solvent extraction, and membranes.

5.1. Ion-exchange

Ion-exchange (Table 2) is an advanced and promising technique in the extraction sector. The mechanism allows for the separation of Li^+ from the hot spring using synthesized resins that have a high selectivity towards Li^+ with low reaction times. The exchanger rejects the other ions present in the hot spring water (e.g., Ca^{2+}, Mg^{2+}, K^+), and the exhausted aqueous flow can be subsequently reintroduced into the subsoil.

A key advantage of the ion-exchange technique is the ability to extract lithium from low-quality water and produce solutions with higher lithium concentrations than traditional methods. These exchangers, also called lithium-ion-sieves, are different resins such as manganese-based (LMOs) and titanium-based (LTOs) resins, known for their high selectivity towards Li^+, high regeneration capacity, and great exchange efficiency, low cost, and easy employment [137]. The theoretical ion-exchange capacities of LMO and LTO materials are approximately 12–52 mg Li^+/g resin (Table 2), which are significantly higher than those obtained in the experimental trials (i.e., 11–33 mg Li^+/g resin, Table 2).

This is mostly since the molar ratio Li/Mn or Li/Ti in the case of LMO and LTOs, respectively, might play a crucial role during the synthesis of the precursor, since different atomic configurations can be obtained, each with a different crystalline structure and consequently a different exchange capacity of Li^+. Therefore, an increase in the Li/Mn ratio in the precursor leads to an increase in the ion-exchange capacity of the resin [138], whereas by exceeding a specific threshold (e.g., 0.8–1.0), the Li exchange capacity decreases [139,140].

5.1.1. Ion-exchanger preparation, structure and regeneration

The ion-exchanger preparation first involves the formation of the precursor resin using the targeted metal ion (i.e., Li^+). Precursor synthesis can occur through different reactions (Table 2), but the most commonly used is the solid-phase reaction, likely due to its simplicity [141]. Among the most widespread precursor structures, $Li_4Mn_5O_{12}$, $LiMn_2O_4$, and $Li_2Mn_2O_5$ (LMOs) or Li_2TiO_3, and $Li_4Ti_5O_{12}$ (LTOs) are known for their high efficiencies (up to 96%, Table 2) [142]. LMOs exhibit typical spinel structures where Li occupies tetrahedral sites, Mn octahedral sites and O face-centered cubic sites [142,143]. LTOs present different structures based on the type of precursor adopted, i.e., with a layer (Li_2TiO_3) or spinel ($Li_4Ti_5O_{12}$) structure [138]. In the layer structure, the first layer (Li layer) is solely constituted by lithium atoms, accounting for 75% of the total atomic composition, whereas the second layer comprises 1/3 and 2/3 of lithium and titanium atoms, respectively [144].

Once formed, the precursor can be immersed in an acid solution (e.g., HCl) where the exchange between the Li^+ and H^+ ions occurs, thus determining the formation of the ion sieves, i.e., hydrogen (H)-MOs or hydrogen (H)-TOs, respectively. Following acid removal, the ion sieve oxides preserve the structural stability of the precursor by showing a high affinity towards the targeted metal ions previously present. The empty sites will allow the reallocation of ions with an ionic radius equal to or smaller than the targeted ions [142,145].

In the case of hot springs, lithium ions will go to reoccupy the empty sites, while the other competitive ions will be rejected due to the higher ionic radius. For instance, Gu et al. [146] and Wei et al. [147] studied the properties of the $Li_4Ti_5O_{12}$ precursor prepared by a solid-phase reaction of Li_2CO_3 and TiO_2, subsequently treated with nitric acid to obtain the $H_4Ti_5O_{12}$. This ion sieve demonstrated an excellent Li^+ selectivity of approximately 59–146 mg Li^+/g resin from a simulated solution.

Table 2
Overview of lithium recovery studies using ion-exchange technique. LMO = manganese-based ion sieves; H-MO = hydrogen-LMO.

Exchanger/ Precursor	Lithium solution (mg/L)	Operating conditions	Theoretical exchange capacity (mg Li/g resin)	Exchange capacity (mg Li/ g resin)	Lithium recovery (%)	Adaptability to hot spring-derived waters	Refs.
Carbon-supported H_2TiO_3	Artificial (29 mg/L)	In-situ polymerization, elution with 0.25 mol/L HCl in 2 h, dissolution <0.8% after 10 sorption cycles	52	29	90	Moderate	[238]
Doped H_2TiO_3-W	Artificial (425 mg/L)	Hydrothermal reaction, elution with 2 mol/L HCl in 12 h; dissolution of 0.6% after 5 sorption cycles	43	33	96	Low-Moderate	[239]
H-MO, LMO	Artificial (100 mg/L)	Hydrothermal reaction, elution with HCl and HNO_3, dissolution of 2–2.5% after 10 sorption cycles	40	25–30	50–80	Moderate	[151]
Granulated $H_4Mn_5O_{12}$	Geothermal water (26 mg/L)	Solid-phase reaction, elution with 0.25 mol/L HCl in 24 h, dissolution <1.2% after 4 sorption cycles	12	11	88	High	[240]
Doped HMO-Al	Shale gas wastewater	Solid-phase reaction, elution with 0.5 mol/L HCl, dissolution ≤2% after 4 sorption cycles	–	29	–	Moderate	[163]

One of the most significant advantages is that the ion-exchanger can be regenerated. Upon resin saturation, the exchanger can be subjected to a regeneration protocol, typically using acidic aqueous fluxes, leading to the formation of lithium salts that are removed, resulting in the formation of regenerated ion exchangers (H-MO or H-TO). Afterwards, the regenerated ion-exchanger can be employed for lithium recovery while maintaining performances for 4–10 consecutive sorption cycles with a residual dissolution below 2.5% (Table 2).

5.1.2. *Operating parameters affecting the ion-exchange process*

During the ion-exchange process with ion sieves, the Li/Mn ratio, calcination temperature, solution temperature, and pH affect lithium exchange capacity. Therefore, a perfect balance of these parameters is necessary to improve performance.

The Li/Mn molar ratio should not be too low to avoid Mn dissolution nor too high to limit lithium recovery from hot springs. For instance, Noerochim et al. [140] prepared different LMOs with a Li/Mn molar ratio of 0.5, 0.8, 1, and 2 using a solid phase reaction at 500 °C for five hours, obtaining the maximum ion-exchange capacity of 6.6 mg Li^+/g resin with the 1 M ratio. Similarly, Shin et al. [139] obtained an exchange capacity of 24 mg Li^+/g resin with LMOs prepared at 500 °C for four hours using lithium and manganese carbonate with a 0.8 Li/Mn ratio. Therefore, Li/Mn molar ratio should be kept between 0.8 and 1.3.

With the rise of calcination temperature during precursor formation, an increase in crystal size hinders lithium recovery efficiencies, since small crystals possess a high specific surface area, which improves the ion-exchange process. Indeed, Zhang et al. [148] studied the effects of calcination temperature in a LTO precursor, demonstrating an increase of crystal size from 100 to 1000 nm with the rise of temperature from 650 to 950 °C, which led to a lithium exchange capacity of about 28 mg Li^+/g•resin at 750 °C (i.e., 90–95% efficiency throughout sorption phases) due to a high specific surface area (i.e., approximately 59 m^2/g•resin). Similarly, Nyarangi et al. [149] obtained a decrease of lithium recovery efficiency from 99 to 94% with the increase of calcination temperature from 650 to 750 °C due to a higher crystal size (i.e., from about 35 to 54 nm) in a Zn-doped Li_2TiO_3.

A pH between 8 and 12 is optimal for the ion-exchange capacity aimed at Li^+ recovery [150]. Low pH values indicate an accumulation of exchanged H^+ ions and limited lithium exchange since acidic solutions limit their recovery, whereas an alkaline pH can lead to a positive effect on the ion-exchange process. High OH^- concentrations neutralize H^+ accumulated in the liquid phase, thus increasing the negative charge on the particle surface [151]. This effect would improve affinity towards positively charged lithium ions and ion-exchange capacity. Recepoğlu et al. [150] showed a significant enhancement of lithium removal from 1 to 82% by increasing the solution pH from 2 to 12, respectively, using doped H-MOs. These materials showed the highest ion-exchange capacity of approximately 15–33 mg Li^+/g resin at pHs of 8–12 due to H^+ neutralization [152,153].

High solution temperatures (e.g., 45 °C) can improve lithium recovery, making the ion-exchange process optimal for hot springs since temperatures can achieve 60 °C [10]. This is mostly due to an increased lithium mobility at high temperatures, which ensures improved ion diffusion in the ionic sieves. Delgado et al. [154] obtained the enhancement of ion-exchange capacity from approximately 2.77 to 9.64 mg Li^+/g resin by increasing the temperature from 25 to 80 °C under alkaline conditions in a geothermal brine. Li^+ exchange capacity of the ion sieve (i.e., 40 mg Li^+/g resin) can be further enhanced at 45 °C by prolonging the extraction time up to 27 h [155].

5.1.3. *Ion-exchange drawbacks*

The ion-exchange methods can be affected by drawbacks. In general, two aspects have to be taken into account, i.e., manganese dissolution in the acidic phase and hydrogen ion-exchange in the hot spring water.

Indeed, during the desorption process of the ionic sieve in the acidic solution, H^+ ions take part in the process by leading to the formation of unstable manganese on the crystal structure surface, thus resulting in the decrease of Mn via dissolution [145]. This effect tends to be more prominent with the increase in the sorption cycles, resulting in decreased resin capacity and lifetime and elevated environmental risks due to manganese toxicity at high concentrations. Disu et al. [141] reported an increase of manganese dissolution using $LiMn_2O_4$ from approximately 5 to 7%, which was associated with a decrease in the ion-exchange resin capacity from about 31 to 19 mg Li^+/g resin after the first and fifth cycle, respectively.

LTOs should be preferred due to their lower dissolution effect under acid treatment and better cyclic stability in the presence of strong Ti—O bond energy than LMOs. Titanium also appears less aggressive to the environment and easily recoverable than manganese, making LTOs environmentally friendly. On the other hand, LTOs show a slower lithium adsorption capacity over time than LMOs.

Therefore, metal-doping can represent a viable alternative to reduce the dissolution of Mn from the structure and, thus, make the material more durable and stable over time [145]. A new type of zirconium-doped H-TO has been recently synthesized using the sol-gel method [156]. The doped sieve demonstrated a high ion-exchange capacity of approximately 69 mg Li^+/g resin using a salt lake brine within 8 h, which decreased to only about 56 mg Li^+/g resin after eight sorption cycles, demonstrating durability and stability [156]. Similarly, Ma et al. [157,158] obtained a high ion-exchange capacity and low dissolution by applying the metal-doping technique with Fe, Ni, and Al on the H-MO and tungsten, zirconium, and cerium on H-TO during a solid-phase

synthesis. Metal-doped H-MOs and HTOs showed an ion-exchange capacity and reduced manganese/titanium dissolution of approximately 21–29 and 35–48 mg Li^+/g resin and 30 and 0.8–1.2%, respectively.

Also, a high Li/Mn molar ratio can be used to contrast the Mn dissolution. Indeed, HMOs can be synthesized with different Li/Mn molar ratios between 1.0 and 2.0, which can lead to the reduction of Mn dissolution from approximately 3% to below 1%. However, above the abovementioned Li/Mn ratios (i.e., 0.8–1.0), the ion-exchange capacity and lithium recovery decrease, thus suggesting that an optimal ratio also to mitigate Mn dissolution should be slightly higher than 1 (e.g., 1.3 leads to an ion-exchange capacity Mn dissolution of about 45 mg Li^+/g resin and 1.7%, respectively) [151].

Several acidic solutions, such as HCl, CH_3COOH and $(NH_4)_2S_2O_8$, can be employed for resin regeneration, thus leading to different Mn dissolutions and Li^+ recovery. Generally low Mn dissolution (i.e., 0.3–1.7%) and high Li^+ recovery (i.e., app. 60–97%) can be achieved using CH_3COOH and $(NH_4)_2S_2O_8$, with acetic acid showing comparable performances also in long-term experiments, as reported by Herrmann et al. [159]. Recently, a novel eluent based on HCl and O_3 has been proposed by Song et al. [160], reporting a decrease of Mn dissolution from approximately 6 to 0.11%, a good structural stability, and an ion-exchange LMO capacity of about 31 mg Li^+/g resin after 10 consecutive cycles by fine-tuning ozone.

During the lithium recovery by ionic sieves, H^+ ions are released into the aqueous solution, thus leading to an acidification of the hot spring water, hindering the ion-exchange mechanism. An alkaline ion-exchange resin can be used since the pH should be kept at neutral values. This would better contrast the acidity during the ion-exchange compared to traditional ammonia-based solutions, which would bring pollution by releasing ammonia nitrogen to the hot spring water being reintroduced into the environment [161].

Table 3
Studies on the use of adsorbents aimed at lithium extraction.

Material/system	Key process parameters	Tested Li concentration / matrix	Mg/Li or competing ions	Lithium recovery/ capacity	Main advantages	Main limitations	Adaptability to hot spring-derived waters	Refs.
Lithium manganese oxide (LMO) powder in multi-stage column (MSC) with fabric filter	Li/Mn molar ratio = 0.8; calcination at 500 °C for 4 h; Langmuir isotherm; pseudo-second-order kinetics	Li-spiked seawater (2–60 ppm); natural seawater	–	23.9 mg/g (spiked seawater); 4–4.9 mg/g (natural seawater)	Avoids binders blocking active sites; practical column operation	Lower performance in real seawater	Moderate	[139]
Doped lithium manganese oxide adsorbents (H1.33RXMn1.67 – XO4; R = Fe, Ni, Al)	Solid-phase synthesis; high-T calcination; acid leaching	Shale gas wastewater	–	20.7–29.0 mg/g (vs. 13.7 mg/g undoped)	Higher capacity; ~30% reduced Mn loss; improved cycling stability	Acid leaching required	Moderate	[163]
β-diketone functionalized brush-shaped polymer	Brush topology; adsorption time 45 min	Geothermal brine (≤100 mg/L Li^+)	High Li^+ selectivity (Kd = 257.74 mL/g)	53.64 mg/g; ~100% extraction; 717× enrichment	Very high capacity and selectivity; fast kinetics; reusability (>10 cycles)	–	High	[165]
Porous LiAl-LDHs granulated with sodium alginate (SDS, OA, SLS templates)	Hydrothermal synthesis; alginate granulation; Langmuir isotherm	Synthetic brine (300 mg/L Li^+); Da Qaidam brine (1.0 g/L Li^+)	Minor effect of other electrolytes	8.48 mg/g (synthetic); 11.8 mg/g (real brine)	Improved porosity; granulated form; pH/temperature tolerant	Moderate capacity; surfactant-dependent performance	Moderate	[169]
Granulated porous mixtures of Li-Al-LDHs and $NH_4Al_3(SO_4)_2(OH)_6$ crosslinked with sodium alginate	Hydrothermal synthesis; lithiation in LiOH; alginate crosslinking in $CaCl_2$; Langmuir isotherm; pseudo-second-order kinetics	East Taigener salt lake brine	Studied anion/ cation interference (not quantified)	9.66 mg/g (synthetic); 9.16 mg/g (real brine); equilibrium in 180 min	Improved applicability; good cycling stability (0.54% dissolution after 10 cycles)	Moderate capacity; longer equilibrium time	Moderate	[170]
Li/Al-layered double hydroxides granulated with crosslinked sodium alginate	One-pot hydrothermal synthesis; alginate as structure modifier	East Taigener salt lake brine (1400 mg/L Li^+)	Electrolyte effects studied (Mg^{2+}, Na^+, SO_4^{2-})	14.5 mg/g (real brine)	Reduced dissolution; improved cycling stability	Tested at high initial Li concentration	Low–Moderate	[171]
Highly porous Li/Al-LDHs derived from multimetallic Al-based MOFs and granulated with EVAH (GLDH; Fe-GLDH; Mn-GLDH)	In-situ MOF-to-LDH transformation; multi-metal doping; polymer granulation; column experiments	Simulated brine; real brine	High Li^+/Mg^{2+} selectivity (separation factor up to 33.67); Mg/Li reduced from 98 to 3	Dynamic adsorption capacity: 1.42–2.23 mg/g (column)	High selectivity; good cycling stability; enhanced Li^+ diffusion	Lower dynamic capacity vs. batch systems	High	[172]
Li/Al-layered double hydroxides with controlled interlayer water content	Tuning interlayer water (5.52–18.18%); neutral desorption; DFT analysis	Qarham Salt Lake old brine	Extremely high Mg^{2+}/Li^+ ratio (>300)	Adsorption capacity increased from 1.05 to 7.89 mg/g with higher interlayer water	Applicable to very high Mg/Li brines; maintained structural stability; enhanced selectivity	Low absolute adsorption capacity at low interlayer water content	Moderate–High	[173]

5.2. Adsorption mechanism

DLE techniques also include the use of adsorbents for lithium recovery (Table 3). Li^+ in the hot spring solution can be adsorbed onto the adsorbent surface by occupying the available pores during the adsorption mechanism. Adsorption should not be confused with the ion-exchange mechanism since an exchange between lithium and hydrogen ions does not occur. The adsorption mechanism is based on electrostatic forces that allow the hydrated lithium ion to bind to the OH^- groups present on the surface of the material, resulting in a reduction of the hydrated shell in favor of binding (Fig. 4c).

Among the available adsorbents, the aluminum-based materials, such as lithium-aluminum layered double hydroxides (LiAl-LDHs) (Fig. 4), are generally employed for lithium recovery from geothermal brines [138,162], due to a strong selectivity towards Li^+ [163]. This material can be easily regenerated after its saturation by desorption with deionized water (i.e., with a low conductivity), thus leading to low costs and reduced environmental risks associated with the use of acid, which is mostly used for ionic sieves instead [158,164]. Beyond inorganic layered materials, β-diketone functionalized brush-shaped polymers have demonstrated remarkably high Li^+ adsorption capacity (i.e., 53.64 mg/g) and selectivity (i.e., K_d = 257.74 mL/g), with fast kinetics (i.e., below 45 min), excellent recyclability (i.e., over 10 cycles), and complete lithium extraction from real geothermal brines at Li^+ concentrations below 100 mg/L [165], highlighting their strong potential for application to hot spring-derived waters.

5.2.1. Adsorbent preparation and structure

LiAl-LDHs (Fig. 4) can be realized through solid-state synthesis, coprecipitation, and hydrothermal methods. In general, Li^+ taken from LiCl or LiOH are intercalated into aluminum hydroxides [166], which can be found in the natural form of certain minerals, such as gibbsite or bayerite (α- and β-$Al(OH)_3$, respectively) [166]. LiAl-LDHs appear as layered crystals formed by metal-hydroxide layers composed of metal-oxygen octahedral units connected by shared edges and extended in two dimensions, with metal cations localized in the center and hydroxyl groups at the six vertices of the octahedron [157,167] (Fig. 4). The chemical formula of LiAl-LDH is expressed as follows:

$$Li \bullet X \bullet 2Al(OH)_3 \bullet nH_2O \quad (8)$$

where X represents the anions (usually chlorine), whereas n is the number of water mols [168], which are inserted between the lithium and aluminum interlayers to form the [157]. The anions between LiAl-LDH layers are combined with the plate layers through electrostatic attraction and hydrogen bonds, which are characterized by the high charge density and anion exchange capacity (Fig. 4). The adsorbent is subsequently obtained via the deintercalation mechanism by eluting the precursor with deionized water.

During deintercalation, Li-ions abandon the adsorbent by leaving octahedral vacancies in the layered structure, which are then reoccupied by Li-ions from the hot spring during adsorption [157]. As mentioned above, the material will be moderately selective towards lithium ions since it shows an ionic radius compatible with the spaces in the material. Therefore, other competitive ions in the hot spring water will be rejected due to a larger ionic radius than the empty adsorbent sites.

5.2.2. Operating parameters and adsorbent performance

To achieve the maximum lithium adsorption capacity by LiAl-LDHs, three critical parameters have to be taken into account: i.e., high salinity, temperature of 40–95 °C, and a minimum lithium concentration (e.g., 100 mg/L) [166].

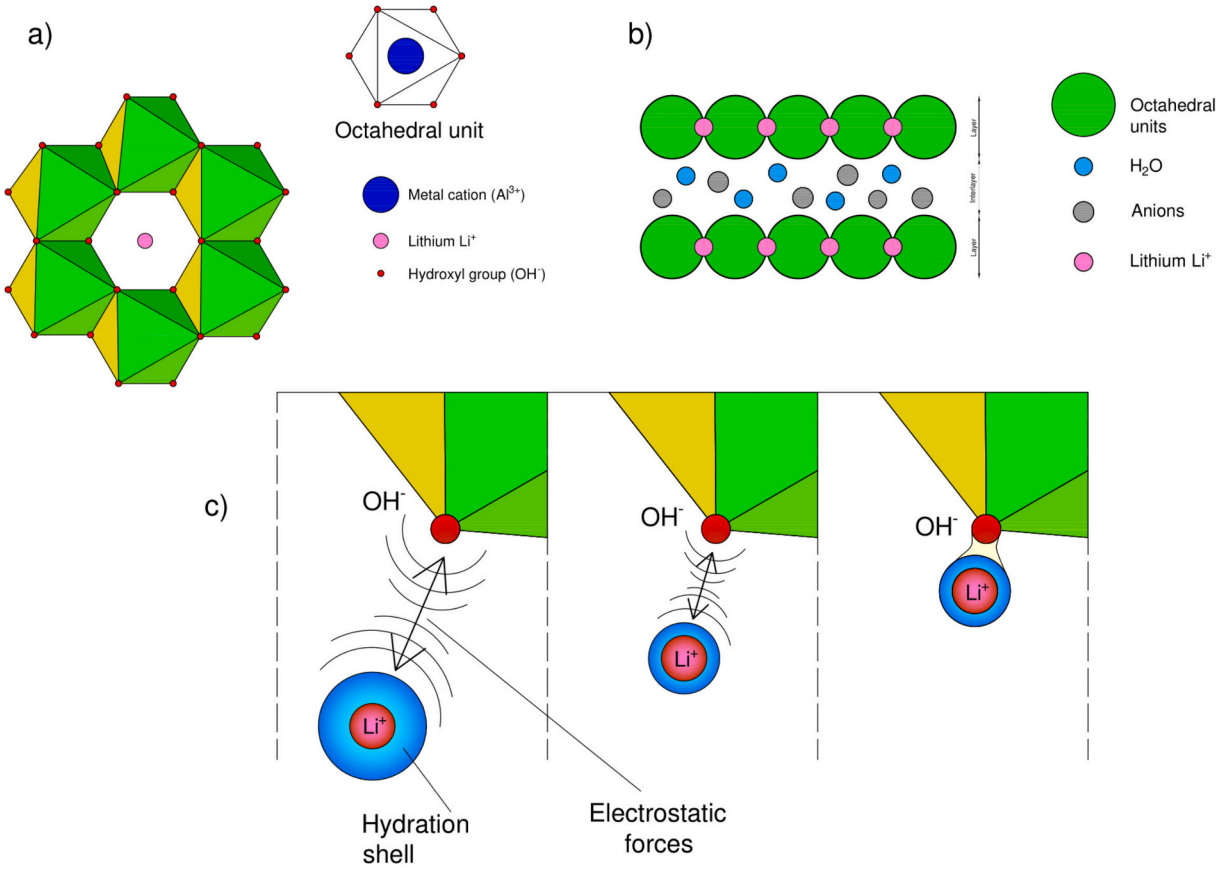


Fig. 4. A schematic representation of (a) the lithium-aluminum layered double hydroxide (LiAl-LDH) structure, (b) intra-layer spaces and (c) adsorption mechanism through electrostatic interaction and reduction of the Li^+ hydration shell.

However, LiAl-LDHs can show a low removal capacity (i.e., below 10 mg Li^+/g adsorbent) in a neutral pH range of application (i.e., 6–8), which is compatible with hot spring solutions [10,138] since adsorbent dissolution can occur at acidic pH [136]. For instance, Dong et al. [169] synthesized a porous LiAl-LDH via a hydrothermal method using surfactants by achieving up to approximately 14.46 mg Li^+/g adsorbent from geothermal brines. Luo et al. [170] and Li et al. [171] showed an improved lithium adsorption of about 7.5–9.7 mg Li^+/g adsorbent using granulated LiAl-LDHs in aqueous solution with the increase of temperature (i.e., 25–45 °C) and optimal pH (i.e., 4–10).

The main limitation of the mentioned studies is a lithium concentration in the water solution of about 0–500 mg/L, and therefore, a preconcentration process (e.g., evaporation) of hot spring thermal water is required, which increases the costs. Metal doping (i.e., with Co, Zn, Mn, Zr, and Ni) represents an alternative to enhance LiAl-LDH properties (i.e., stability) and overcome its low adsorption capacity by altering the interlayer spacing and surface charge of the adsorbent [157].

Doped LiAl-LDH (e.g., with manganese) showed an enhanced lithium adsorption by achieving approximately 7–13 mg Li^+/g adsorbent in brine and a high adsorbent stability above 5 consecutive adsorption-desorption cycles (Al dissolution below 0.2%) [172,173]. Also, here, increased temperature (i.e., 25–45 °C) and a high Li/Mn ratio can positively influence the adsorption mechanism. Also, the enhancement of interlayer water content from about 6 to 19% can significantly improve the lithium adsorption (up to 8 times) without compromising stability [173].

High concentrations of competitive ions (e.g., Mg^{2+} and Ca^{2+}) during the adsorption hinder the selective and extractive process compared to ion exchangers with high selectivity resins; consequently the Mg/Li and Ca/Li ratio is a parameter to be considered. The Mg^{2+} ion has similar ionic dimensions to the Li-ion, creating interference during extraction. Furthermore, its greater charge causes the Mg^{2+} to hydrate more strongly, creating hydration shells and more stable and stronger bonds with the adsorbent material, removing sites to the Li^+. On the other hand, the Ca^{2+} is less competitive than the Mg^{2+}, exhibiting a lower affinity for small sites as predisposed to the Li^+ ion. However, high concentrations of Ca^{2+} in the aqueous solution can still occupy the active sites, especially if the adsorbent material is not highly selective. A pre-removal of the Mg^{2+} ions or Ca^{2+} ions can be carried out using precipitants, achieving high performance [127,174]. NaOH, CaO, $Ca(OH)_2$, and Na_2SO_4 are the most commonly used chemical precipitants for precipitating the previously mentioned competitive ions without interfering with the Li^+ ions in solution under optimal conditions [141]. Recently, some researchers have investigated the use of new precipitants that allow a more selective and rapid removal of Mg^{2+} without affecting the recovery of Li^+. For instance, sodium metasilicate nonahydrate has been used to effectively precipitate Mg^{2+}, reaching an efficiency of 99.94% and a reduction of the Mg/Li ratio from 30 to 0.022 [175]. In addition, another novel precipitant is $NH_4MgPO_4{\cdot}6H_2O$ used in a struvite process with tri-ammonium phosphate trihydrate for the removal of Mg^{2+} in a simulated brine reaching 99.71% efficiency [176]. Chemical precipitation is used on various types of brines; nevertheless, the technique can also be used for magnesium and calcium aqueous solutions derived from hot springs with a chemical composition similar to brines. Alongside chemical precipitation, there are many other methods that can be used to reduce the Mg/Li or Ca/Li ratio, such as the use of nanofiltration membranes, selective resins, or selective adsorbents. However, the high costs at large scale and development stages lead to prefer conventional methods.

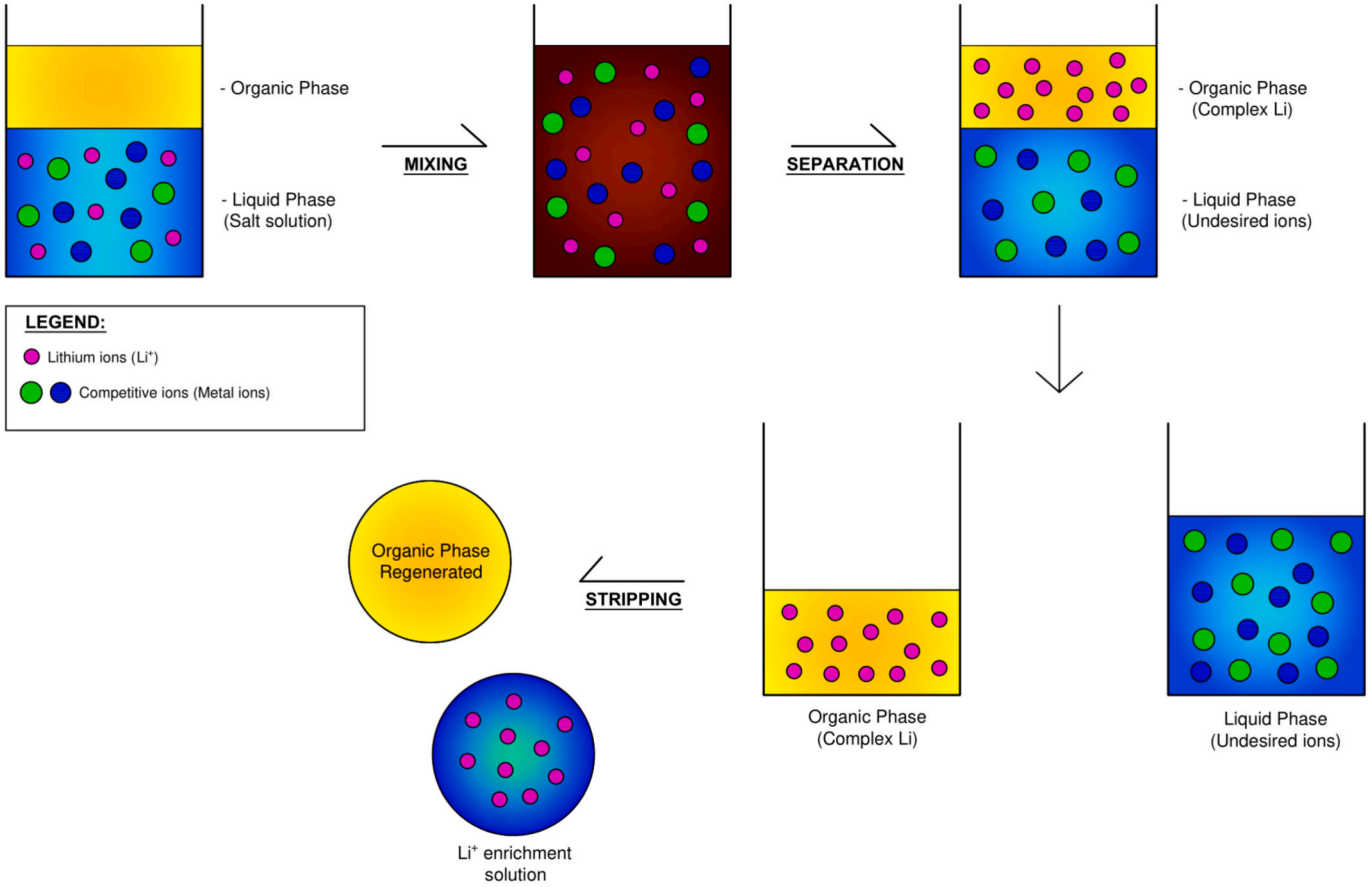


Fig. 5. Phases involved in the solvent extraction process (i.e., mixing, separation, and stripping).

5.3. Solvent extraction

Solvent extraction (Fig. 5 and Table 4), also called liquid-to-liquid extraction, is a mechanism within the DLE family that extracts lithium by removing impurities. The process involves two immiscible liquid phases, i.e., an organic phase with the presence of the organic solvent used for lithium recovery, and an aqueous phase composed of the metal solution from the hot spring-derived brine. Whereas the two phases are mixed, the lithium ion reacts with the organic solvent, forming Li-ion complexes. Afterwards, Li-ion complexes and some residual impurity metals are transferred to the organic phase.

Fig. 5 shows a schematic representation of the solvent extraction process. After the mixing (Fig. 5), the two phases are separated, leaving in the aqueous phase all the competing ions present in the brine (i.e., Ca^{2+}, Mg^{2+}, Na^{+}, etc.) and in the organic phase a high lithium concentration. Subsequently, the organic phase is removed (Fig. 5), typically with water or acid solutions, to remove lithium in high concentration by obtaining an enriched solution. After stripping (Fig. 5), the organic phase is regenerated and reused for a new extraction cycle. The solvent extraction method is applicable with low operating costs, facility, and high efficiency [17].

However, high Mg/Li or Ca/Li ratios can still interfere with solvent extraction. These divalent ions complex strongly with the organic extractant due to their high hydration energy, occupying most of the extractant and reducing the efficiency of Li transfer from the aqueous phase to the organic phase. In addition, divalent ions that pass into the organic phase interfere with the Li stripping phase, resulting in their accumulation in the concentrated Li solution as impurities, leading issues with the precipitation of Li_2CO_3 or LiOH. Consequently, divalent ions (Mg^{2+} and Ca^{2+}) have to be removed beforehand in order to maintain the efficiency of the solvent extraction steps [16]. As mentioned previously, chemical precipitation techniques using common or new precipitants appear to be one of the most advantageous solutions for reducing the Mg/Li or Ca/Li ratio.

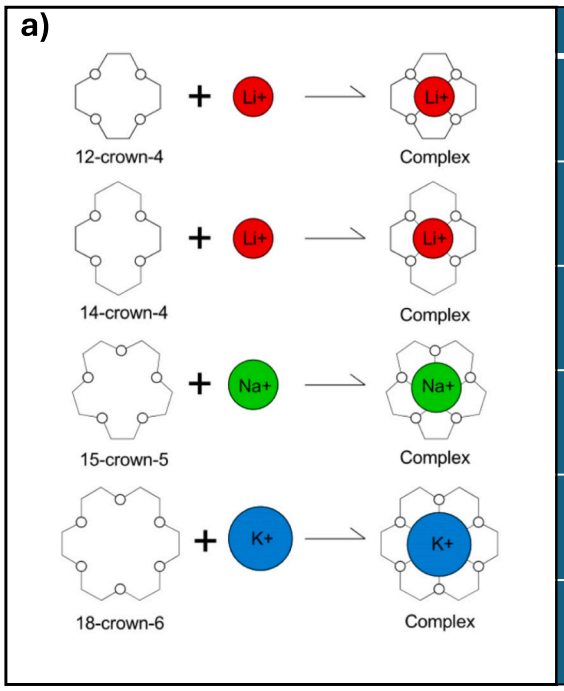
The extraction efficiency is affected by selecting of the appropriate extractant to separate and recover Li-ions from the solution [177]. Nonetheless, the choice of solvent to be used in the organic phase is also associated with different costs and environmental risks connected with its use. Kerosene has recently been widely used as an extracting solvent for Li-ion recovery. Still, its flammability effects and other risks associated with its usage have led the solvent extraction world to explore novel, safer, and environmentally friendly solvents [178]. Therefore, more eco-friendlier solvents are investigated here, i.e., chelating, organophosphorus, and ionic systems.

5.3.1. Chelating systems

Among chelating solvents, crown ethers demonstrated strong binding tendencies and extractive capacity towards Li^{+}, making them a promising candidate in this sector. Crown ethers are a family of cyclic polyethers in which the fundamental structural unit, represented by -OCH_2 CH_2-, is repeated to form these compounds. However, their name derives from their stable configurations that assume the shape of a crown. Negatively charged oxygen atoms easily interact with positively charged alkali metal ions, such as Li^{+}, to form stable complexes and structures [151]. Oxygen atoms form a circular cavity with a size that allows the encapsulation of one metal ion rather than another through dipole-charge electrostatic interactions [179]. Other donor atoms, negatively charged, can be used in the system of crown ethers, such as N and S. Competitive ions in the salt solution that have very similar chemistry to Li^{+}, such as Na^{+} and Mg^{2+}, can hinder the recovery process and change the selective order due to similar ionic radii. For optimal recovery, the Na/Li and Mg/Li ratios should be low, although solvent extraction technology today achieves significant results even for high ratios. Fig. 6a shows a schematic representation of the most stable

Table 4
Studies on solvent extraction techniques aimed at lithium extraction.

Extractant system	Key extraction parameters	Tested brine/ impurity info	Lithium extraction performance	Main advantages	Main limitations/ issues addressed	Adaptability to hot spring-derived waters	Refs.
Neutral organophosphorus: TOP + $FeCl_3$ in MIBK	Optimized Fe/Li; phase ratio; stripping; single-stage	Salt lake brine; Li/Mg evaluated	85% Li extraction (single stage); Li/Mg = 5842	Exceptional Li/Mg selectivity; reduced extractant dissolution	Extractant loss addressed but remains a concern	High	[182]
Acidic organophosphorus: D2EHPA + kerosene/ vegetable oil	O/A = 1:1; 30 min; 1 M; 300 rpm; Taguchi L8	Sidoarjo mud leachate	Optimized Li extraction; ratio contribution 67.22%	Simple, mature chemistry	Li/Mg selectivity not reported	Moderate	[184]
PC88A vs HBTA (β-diketone)	pH; O/A (1/1–15/1); McCabe–Thiele	Not specified	98%: 6 stages (PC88A) vs 1 stage (HBTA)	Very high stage efficiency (HBTA)	Higher extractant cost	Moderate	[185]
TBP–$FeCl_3$	O/A = 1:1; Fe^{3+} 15–20 g/L; 0.05 M HCl; 4 extraction stages; scrubbing (4 M LiCl); stripping (2.5 M HCl, 10 stages)	Chilean brine (low Cl^{-}, high Ca^{2+})	74.2% (4 stages); 80.3% recovery; 25.3 g/L Li^{+} in strip	Works in low-Cl^{-}/ high-Ca^{2+} brines; strong impurity removal	Multistage, chemically intensive	High	[186]
TBP in sulfonated kerosene (SK)	12-stage counter-current; stepwise stripping; $FeCl_3$ regeneration	LFP battery leachate	>99% overall Li recovery; 3.059 mol/L Li^{+} in strip	Closed-loop; no pollutant emission	Recycling scope, not natural brines	Low–Moderate	[189]
Mixed extractants: TBP + P204 + $FeCl_3$ in kerosene	40% TBP + 10% P204; Fe^{3+}/Li^{+} = 1.6; O/A = 1; water stripping	Salt lake brine; Mg^{2+} scrubbing	52.71% (single stage); Mg^{2+} removal 90.64–95.37%	Improved $FeCl_4^{-}$ stability; reduced TBP degradation	Moderate single-stage extraction; Cl^{-} dependence	Moderate–High	[192]
Functionalized IL (β-diketone + [C_6mim]Cl) in 2-octanone	Single-stage; LiCl washing; HCl stripping; regeneration	Real Chaka brine (high Na/Li)	94% single-stage; >98% Na^{+} wash; >99% Li^{+} strip; ~86% after 10 cycles	High efficiency without co-extractant; good cycling	IL synthesis; cost/viscosity not discussed	High	[199]
[AMIM][Tf_2N]–TIBP–DCM (IL + organophosphate + diluent)	Single-stage; synergistic extraction; QC-guided mechanism	Mg^{2+}-rich brine with Na^{+}/K^{+}	96.87% single-stage; βLi/Mg = 1161.94; βLi/Na = 76.74; βLi/K = 1263.46	Outstanding selectivity; molecular-level understanding; synergy	Use of DCM; scalability/cost not discussed	High	[200]



b)

Crown ether	Selectivity order	Li^+/Na^+ ratio
14-crown-4	$Li^+ >> Na^+ >$ (No K^+, Rb^+ ,Cs^+)	20
15-crown-4	$Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$	3.5
13-crown-4	$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	2.3
12-crown-4	$Li^+ > Na^+ > K^+ > Rb^+ \geq Cs^+$	1.7
Benzo-14-crown-4	$Li^+ > Na^+ > K^+ > Rb^+$ (No Cs^+)	4.7
Benzo-12-crown-4	$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	1.8

Fig. 6. Illustration of (a) stable complexes and connected alkaline metal ions using oxygen atoms as donors and (b) the crown ethers for recovering Li-ions from solutions.

complexes and connected alkaline metal ions using oxygen atoms as donors, compatible with the diameter of the cavity.

Referring to Li^+, 12-crown-4, 14-crown-4 and 15-crown-4, show the best selectivity towards lithium ions with significant binding capacity and appropriate cavity size [178], furthermore, with high Li^+/Na^+ ratios. Fig. 6b shows the crown ethers most favorable for recovering Li^+ from solutions, as well as the selective order and Li^+/Na^+ ratio [127,180].

As mentioned above, the recovery efficiency of Li^+ depends on the cavity size of the crown ether; nonetheless, the type of donor atom also influences the recovery efficiency. Oral et al. [181] analyzed the effects of different donor atoms (i.e., O, N, and S) within the crown ethers, showing that when O is replaced by N and S, there are higher stabilities of the complex as well as a better metal-donor interaction leading to improved selectivity. Despite the advantages associated with the use of crown ethers for the extraction of lithium, polluting and corrosive effects related to these chemicals have been found in this field, which have led to a delay in their commercialization and actual use only at the laboratory scale. Future research should focus on the realization of more environmentally friendly crown ethers.

5.3.2. Organophosphorus systems

Organophosphorus solvents are widely used for the extraction of Li^+ from aqueous solutions due to their binding strength and low cost, allowing the formation of stable metal ion complexes. The separation mechanism is based on the selective coordination of the P═O groups with metal ions to form these stable complexes through ion exchange or electrostatic interactions [182]. Organophosphorus solvents are classified into acidic, such as di(2-ethylhexyl) phosphoric acid (D2EHPA) and (2-ethylhexyl)phosphonic acid (PC88A), and neutral, e.g., tri-n-butyl phosphate (TBP) and tri(2-ethylhexyl) phosphate (TOP) [182,183]. Li-ion recovery of about 67% was obtained by Juliastuti et al. [184] from a leaching lithium-rich solution area using D2EHPA as extracting solvent, whereas Seo et al. [185] achieved about 98% of lithium extraction using 4,4,4-Trifluoro-1-phenyl-1,3-butanedione and PC88A after 1 and 6 cycles, respectively.

Metal chlorides can be combined with other organophosphorus solvents to improve the selectivity and extraction efficiency of Li^+ as a co-extraction agent [186]. Li and Binnemans [187] investigated several chloride metals (i.e., $CuCl_2$, $AlCl_3$, $FeCl_3$, $InCl_3$, and $SnCl_4$) for lithium extraction from aqueous salt solution with TBP as the organic extracting solvent, demonstrating an improved performance in the presence of $FeCl_3$ (i.e., 65–83%). This result was in agreement with other studies conducted with TBP and $FeCl_4^-$ [186,188,189].

The extraction mechanism is explained by Eq. (9) [186], as follows:

$$Li^+_{(aq)} + Fe^{3+}_{(aq)} + 4Cl^-_{(aq)} + 2TBP_{(org)} \rightleftharpoons \left[LiFeCl_4(TBP)_2\right]_{(org)} \quad (9)$$

where the stable complex and the co-extractor are $[LiFeCl_4(TBP)_2]$ and $FeCl_3$, respectively. However, a high concentration of Cl^- (i.e., > 6 M) is necessary to form tetrachloroferrate in the system, which is employed in the stripping phase to recover Li^+ by obtaining LiCl in the liquid phase (Eq. (10)).

$$LiFeCl_4 \bullet nTBP_{(org)} + HCl_{(aq)} \rightleftharpoons HFeCl_4 \bullet nTBP_{(org)} + LiCl_{(aq)} \quad (10)$$

Acidic conditions are required to prevent the loss of Fe^{3+} during the process [190], as well as an increase in H^+ concentration during the stripping phase, can improve the lithium stripping efficiency of Li up to 99% after a few cycles [191]. However, a long-term contact of TBP with an acid (e.g., HCl) would cause deterioration of the organic solvent [192]. The regeneration of the organic phase is generally performed with NaOH after stripping with HCl.

Further drawbacks associated with highly acidic environments can lead to significant corrosive effects on the equipment, as well as potential health risks for operators in contact with those solvents [193]. Hence, finding safer and more sustainable solvents and trying to replace acids during the stripping phase with less aggressive compounds is necessary.

5.3.3. Ionic systems

Ionic liquids are constituted by organic cations and organic or inorganic anions, whose structure and properties can establish the target ions to separate [194]. Ionic liquids are used today as eco-friendly alternatives to traditional organic solvents in solvent extraction due to their low flammability, non-volatility, selectivity, thermal stability, high

efficiency, and sustainability [195]. In addition, ionic liquids can be regenerated and reused after metal extraction, thus reducing the overall operating costs [196].

In the context of lithium extraction from aqueous sources, various ionic liquids can be used, such as $[N_{4444}][DEHP]$, $[N_{4444}][EHPMEH]$, and $[C_4mim][PF_6]$, which are known for significant Li-ion extraction efficiencies. For instance, Shi et al. [193] used $[N_{4444}][DEHP]$-based ionic liquid for extracting approximately 45–93% of lithium ($[Li^+]$ = 0.5 g/L and [HCl] = 0–0.5 M; [functionalized ionic liquids] = 1.06 M; at 20 °C) with a stripping recovery above 90% in the presence of 0.5 M HCl. Likewise, Zhao et al. [197] and Shi et al. [198] employed $[N_{4444}][EHPMEH]$ and $[C_4mim][PF_6]$, respectively, achieving Li^+ extraction higher than 90% and approximately 94% during stripping recovery with HCl. The regeneration of ionic liquids is necessary to allow their reuse after the stripping phase. Salt alkaline solutions can be used for regeneration, allowing Li^+ extraction efficiencies to remain high even after several extraction cycles [199,200].

5.4. Membrane-based applications

The membrane application is a well-established technique for lithium extraction in industrial processes due to low energy requirement, high recovery efficiency, good working condition adaptability, and elevated mechanical properties [201]. Feed enrichment and lean raffinate techniques, which are summarized in Table 5, are generally used based on lithium concentration improvement and ion selectivity [141], respectively.

5.4.1. Feed enrichment technology

Feed enrichment techniques can be used to generate a hot spring-derived brine containing a high concentration of lithium ions. Among these technologies, nanofiltration and distillation/crystallization were applied for lithium recovery [202,203].

Membranes with pore sizes between sub-nanometers and a few nanometers have garnered substantial interest for Li recovery [204]. The extraction mechanism of a nanofiltration membrane (Fig. 7) is based on the Donnan exclusion principle [205], which rejects multivalent ions (e.g., magnesium, approximately 90–95%) in favor of monovalent cations (e.g., lithium, approximately 10–20%) in the presence of a charged membrane (positive or negative) [201]. In addition, hydrated divalent ions in the salt solution have ionic radii much larger than the pore size, thus being blocked on the membrane surface (Fig. 7). Several fabrication strategies have been developed to optimize the membrane selectivity and permeability, such as polyamide layers and multi-walled functionalized carbon nanotubes [206]. The use of anchoring ionic liquids or cationic polymers (e.g., polyethylene-imine, quaternary compounds) can improve lithium/magnesium separation to 33.4 [207]. Although nanofiltration is environmentally friendly with discrete lithium selectivity, the costs related to membrane synthesis and fouling drawbacks are still challenging.

A novel technology based on distillation and crystallization was proposed to overcome nanofiltration issues. As the name suggests, during this technique and in the presence of a polypropylene membrane, solution ions are concentrated by evaporation and vapor collection (distillation), with a subsequent recovery of salts in crystal form (crystallization) [208]. Although distillation/crystallization technology has succeeded in achieving lithium recovery, this technique highly relies on increased LiCl concentration up to 10–14 mol/L [209], thus requiring a longer time and more energy than other technologies (e.g., lean raffinate). Further drawbacks can be high crystallization temperatures needed for the salt precipitation, which can affect its morphological characteristics and increase operating costs. Also, low ion selectivity and membrane wettability can occur.

5.4.2. Lean raffinate techniques

Lean raffinate membranes offer a promising strategy for selective lithium extraction from hot spring water, which is rich in competing cations, such as calcium and magnesium. These membranes rely on ionic liquids, ion-imprinted, and ion-exchange strategies [141].

Liquid-supported membranes show an organic phase facilitating ion transfer between feed and stripping solutions, thus providing a high selectivity towards Li-ions while minimizing solvent use and energy consumption [210]. However, low recovery efficiency (i.e., 7.8–18%) [210] can be affected by the carrier choice and the adsorbent internal arrangement (i.e., 5–7.5 Li/Na or K with hollow fibers) [211]. Also, liquid-supported membranes cope with long-term stability and solvent loss, producing scarce industrial implications.

A different strategy to address solvent drawbacks involves ionic structure incorporation within the membrane matrix, enhancing sorption (i.e., approximately 26 mg Li^+/g membrane) and permitting efficient regeneration [212]. This would overcome the limitations of crown ether membranes (i.e., Mg/Li ratio below 1) [213] in hot spring-derived brine (i.e., high Mg/Li ratio) due to improved selectivity (i.e., Li/Mg separation factor = 193) [212] and reusability. However, future efforts

Table 5
Studies on membrane-based techniques aimed at lithium extraction.

Membrane-based technique	Feed solution	Operating conditions	Recovery/rejection (%)	Adaptability to hot spring-derived waters	Refs.
Nanofiltration	Synthetic lithium-containing solution	Temperature: 20–50 °C; Flow rate: 70 mL/min	Lithium rejection <10%; Ca^{2+} and Mg^{2+} rejection >30%	Moderate	[208]
Distillation/crystallization	Brine solution	Temperature: 20–60 °C; Flux: 1.3–4.2 L/h	Lithium recovery 15.1 kg/h	Moderate	[209]
Polyamide composite nanofiltration	Seawater with lithium	Pressure: 0.3 MPa; Temperature: 25 °C	Rejection rates ($MgCl_2$ – LiCl) up to 47.5%; Mg/Li: from 20 to 7.7	Moderate	[206]
Ion-selective membrane	Simulated brine	Temperature: 25 °C	Mg/Li separation factor up to 33.4, $MgCl_2$ and LiCl rejection 98.5 and 46.2%, respectively	Moderate–High	[207]
Polydopamine and polyethylenimine membranes	Industrial wastewater	Flux: 21.33L/m^2·h	Lithium permeability: 95%; Mg^2/Li^+: from 30 to 4.1	High	[241]
Quaternized bipyridine membrane	Salt Lake brine	Temperature: 30 °C; Flow rate: 0.67 L/min	$MgCl_2$ rejection: 92%; Mg^2/Li^+: from 50 to 8.5	High	[242]
Nanofiltration membrane	Salt solution	Pressure: 8–9 bar; Temperature: 25 °C	$MgCl_2$ and LiCl rejection 74.4 and 84.0%, respectively; Mg^2/Li^+: from 30 to 60	Low	[243]
Sodium periodate-oxidized polydopamine	Lithium-rich brine	Temperature: 25–65 °C (synthesis and reflux)	Mg^2/Li^+: 6.71; sorption capacity: 42.6 mg Li^+/g membrane	High	[244]
Magnetic graphene oxide surface lithium ion-imprinted membrane	Synthetic lithium solution	Temperature: 25–70 °C	Sorption capacity: 31.24 mg Li^+/g membrane; regeneration performance: 91%	Moderate	[245]
Ion-imprinted polymers loaded on pretreated vermiculite	Synthetic solution	–	Lithium separation factor: 3.5; sorption capacity: 2.9 mg Li^+/g membrane	Low	[246]

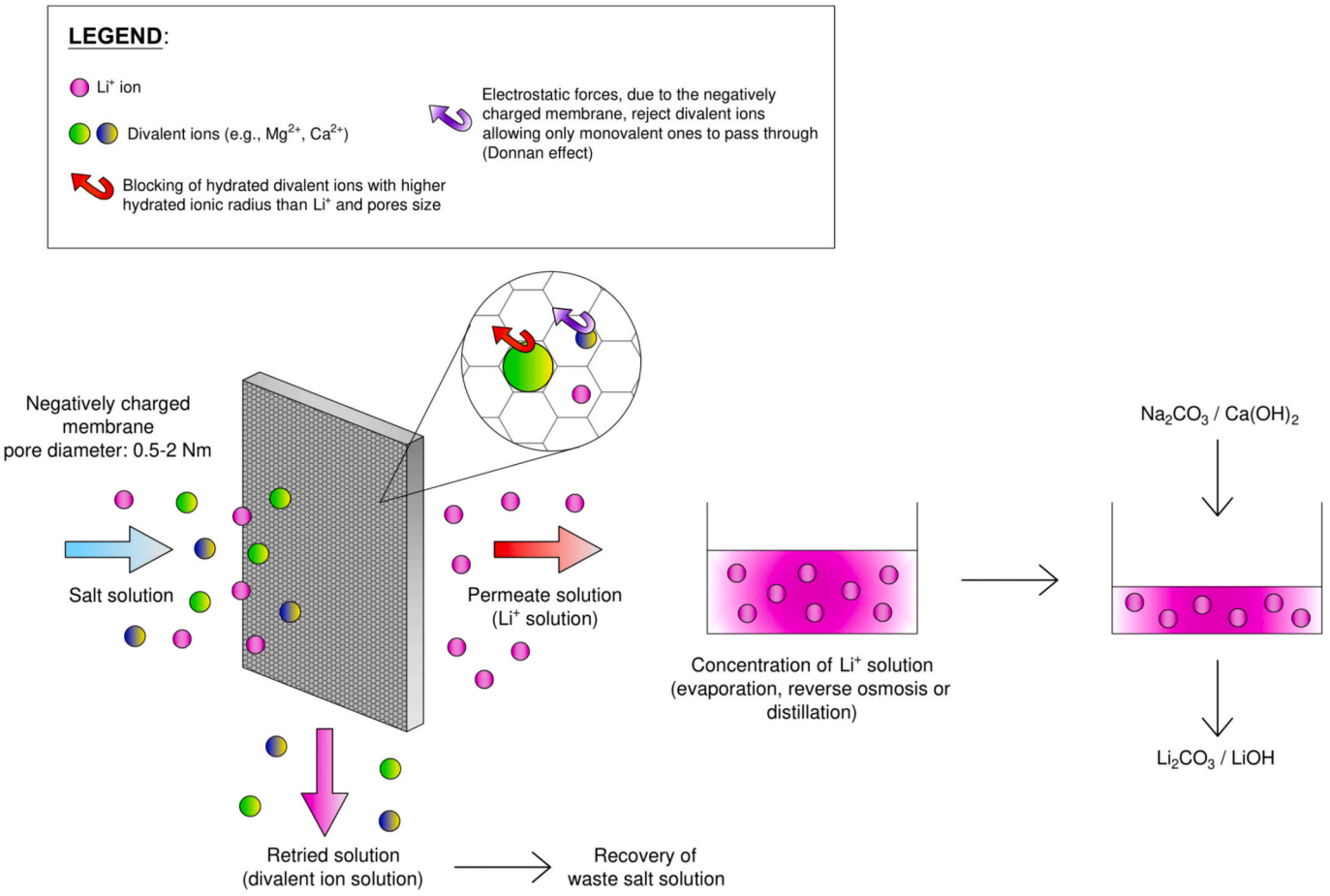


Fig. 7. Lithium extraction via the nanofiltration membrane process and the main related mechanisms.

should focus on cost-effective synthesis and developing membrane structures to enhance separation efficiency without hindering binding sites.

Compared to imprinted membranes, ion sieve powder sorbents can be shaped into membranes, enhancing separation and retention (i.e., about 28 mg Li^+/g membrane and 770 mg/m^2, respectively) [214,215], making this material ideal for continuous lithium extraction and industrial applications. However, a key challenge is the reduced retention capacity caused by polymeric blockage of the binding sites (e.g., electrospinning) [216].

5.5. DLE technique comparison

DLE methods (Table 2, 3, 4 and 5), such as ion-exchange, adsorption, solvent extraction, and membrane-based applications, can be feasible solutions to extract lithium from hot springs with high recovery.

However, as reported in Table 6, the geochemical characteristics can generally affect the applicability of DLE techniques to hot springs. In addition to brine chemistry, the elevated temperatures and variable pH conditions characteristic of hot springs can further influence the stability and long-term performance of DLE materials originally developed for conventional salt-lake brines. Thermal stress, coupled with acidic or alkaline regeneration environments, can accelerate structural degradation, metal dissolution, fouling, or chemical aging, particularly for ion-exchange resins and membrane-based systems.

Ion-exchange resins (i.e., LMOs and LTOs) show high selectivity towards Li-ion. However, Mg^{2+} competitors strongly influence ion-exchange resin efficiency, thus limiting their long-term stability, specifically for LMOs under acidic regeneration. Adsorbents (e.g., LiAl-LDHs) are environmentally friendly and can be regenerated using mild conditions, but LiAl-LDHs have low adsorption capacities under pH 6–8 and require pre-concentration steps to improve their effectiveness. Solvent extraction is attractive due to the ability to be performed under high Mg/Li ratios, combining metal chlorides with organophosphorus

Table 6
Comparison of direct lithium extraction (DLE) techniques applied to hot springs. Symbols indicate relative performance: "+" = low, "++" = moderate, "+++" = high.

Technique	Performance at low Li concentration	Tolerance to Mg/Ca interference	Acid/alkali stability	Main drawbacks in hot spring systems
Ion-exchange (LMOs, LTOs)	+++	+	++	Mn dissolution during regeneration, synthesis cost
Adsorbents (LiAl-LDHs)	++	+	+	Low adsorption capacity; limited cycles without doping
Solvent extraction (chelating, organophosphorus and ionic systems)	++	++	+	Solvent loss, hazardous residues
Membrane-based applications (feed enrichment and lean raffinate techniques)	++	++	++	High cost, fouling

solvents, but requires alkaline/acidic regeneration, posing environmental concerns due to organic degradation. Membrane-based technologies offer promising selectivity by incorporating pre-concentration and separation phases, but can be limited by fouling and high costs.

This comparison highlights that no single DLE pathway is universally optimal for hot spring-derived brines, and the development of materials with enhanced acid/alkali resistance and long-term durability remains a critical research priority. Accordingly, DLE technologies originally developed for conventional salt-lake brines may require material redesign or operational adaptation for hot spring applications, including improved thermal stability, acid/alkali resistance, and long-term cycling durability.

6. Critical discussion

6.1. Environmental, economic, and technological barriers

Although lithium recovery technologies (e.g., evaporation, DLE techniques) showed high performances (i.e., 95–99%) [217] (see Sections 4 and 5), their long-term sustainability, economic feasibility, and technology barriers should be deeply assessed for thermal springs.

Evaporation, chemical precipitation, and membrane-based techniques lead to the generation of a large amount of spent brine after lithium recovery. An incorrect hot spring-derived brine management, involving the reinjection in local springs or aquifers, would negatively affect the natural geochemical equilibrium, thus impacting future recovery cycles and threatening aquatic biodiversity due to toxic by-products [97]. Similarly, the solvent extraction and ionic liquid processes generate a large volume of hazardous organic compounds (see Section 5.3). Evaporitic technologies are also affected by further drawbacks such as water loss, carbon dioxide emissions, long evaporation time, and land usage (see Section 4.2). Manganese dissolution in the acidic phase and hydrogen ion-exchange in the hot spring water can further limit the employment of ion-exchange techniques (see Section 5.1.3). The recovery of the adsorbent used, which could be dispersed into the environment, should also be considered for lithium recovery through adsorption. In addition, membrane-based processes can be energy-prohibitive, especially for treating hot spring water due to low-to-moderate Li-ion content (see Section 5.4).

At this scope, reverse osmosis can become a possible sustainable lithium source due to dual benefits, i.e., recovering Li while producing freshwater, primarily when water scarcity occurs in lithium-rich territory [13]. On the other hand, lithium-depleted brine could be categorized and protected as a further water resource instead of being treated and classified as a mineral resource. Therefore, site-specific environmental impact and mitigation strategies should be further implemented to fill this research gap.

Economic feasibility is a basic hindrance to the commercial application of advanced lithium recovery. By roughly comparing lithium production costs, salt lake brines and seawater use can reach approximately 2 $/kg and 80 $/kg, respectively, due to different initial Li-ion concentrations [13]. Therefore, an extraction cost for hot springs should be expected in the above-mentioned range. Also, high capital expenditure is required in most modern systems, mainly due to the cost of particular materials and special equipment [218]. For instance, ion-exchange techniques revealed high efficiency and selectivity for brines and salt lake waters. However, LMO sieves are difficult to commercialize since their synthesis is energy-intensive and, therefore, cost-prohibitive on a large scale (see Section 5.1). Again, membrane-based systems are technologically appealing but are affected by drawbacks, such as membrane deposition and flux reduction, thus increasing the operating costs (see Section 5.4).

Most novel lithium recovery applications were performed on a laboratory or pilot scale for salt lake water and reverse osmosis brines [219]. Being power-intensive, expensive, and economically uncompetitive unless innovative, the recovery of Li-ions from hot spring-derived brines in a large-scale application remains challenging. Technical barriers can occur due to lithium selectivity, material stability, and equipment durability. Lithium recovery is involved in a specific range of Mg/Li ratios or Li-ion initial concentration [217]. Adsorbent stability is affected by regeneration and competing cations-induced degradation [220]. Due to salt feeding, equipment degradation is an issue in solvent extraction processes and membrane systems, and powerful pre-treatments are consequently required.

Notwithstanding, opportunities for innovation can persist. Considering that a thermal spring can generate approximately 16 thousand m^3/d of water, and over 30 thousand hot springs are present worldwide, about 500 million m^3/d of thermal spring water is released. This entails hundreds of tons of Li worth over 50 million $/d [201]. Getting even a little bit of this would revolutionize the economic scene. This would need integrated system redesigns where hot springs are not viewed only as “thermals”. Electrochemical techniques have lately been investigated for lithium recovery, such as those employed in batteries, in which electrodes capture Li-ions from the feed and discharge them into an extracting solution [221]. Integrating such systems with renewable forms of energy (e.g., solar power) can decrease excessive energy consumption, positively impacting the environment.

6.2. Future directions

Two research directions are particularly relevant to turning hot-spring lithium recovery into a deployable option: geological prospecting of high-potential systems and integrating thermal energy into extraction processes. The first direction moves beyond static concentration measurements to prioritize lithium mass flux (i.e., the product of concentration and discharge rate), temporal variability, and hydrothermal controls, such as structural settings, fault geometry, heat flow, and lithology. The application of multi-tracer hydrogeochemistry (e.g., co-enrichment patterns, such as Li-B-Rb-Cs, and isotopic/trace-element fingerprints) can help distinguish fluid sources and mixing, reduce exploration uncertainty, and guide pilot-site selection and sampling density [9,114,222,223]. The second direction focuses on reducing overall energy demand. Research should focus on process intensification and heat cascading to support pre-concentration (e.g., thermally driven membrane processes), enhance sorption/ion-exchange kinetics, facilitate regeneration steps, and provide heat for downstream conversion (i.e., Li_2CO_3/LiOH) where applicable. Design principles and pilot-scale evidence from geothermal brines (i.e., continuous operation, brine reinjection, integrated techno-economic analysis, life cycle assessment) provide transferable lessons for hot-spring contexts [224–226]. For instance, Liu et al. [226] decreased the costs by six times the 2023 market price to $ 4.1/kg LiOH•H_2O after a techno-economic assessment using electro-driven Li extraction on geothermal brines. A life cycle assessment previously showed that DLE can decrease the carbon footprint by approximately 49% as CO_2eq per ton of battery grade compared to conventional methods [227]. These directions should be complemented by field-representative pilots with real waters, long-term cycling/durability tests (i.e., thermal stress, pH swings, competing ions), and integrated techno-economic and life-cycle assessments under realistic brine management and environmental protection constraints.

7. Conclusions

The annual growth of lithium demand in many economic and industrial sectors for energy and storage applications, such as in the electric-automobile sector for Li-ion batteries, currently presents a challenge to the research of new exploitable natural resources for lithium extraction. This review article focused on hot springs as a new unconventional resource that can be used for lithium extraction to supplement the previously exploited conventional resources (i.e., brines and ores), providing geological information and potentially applicable extraction techniques for lithium recovery. Globally, lithium in hot

springs ranges from approximately 0.1–250 mg/L, exceeding 400 mg/L in areas with high hydrothermal activity and mineral alterations. The existing lithium recovery techniques can be used to separate the Li^+ from other competitive ions (i.e., Ca^{2+}, K^+, SO_4^{2-}, HCO_3^-, and Na^+). High lithium recovery efficiencies, comprised between 90 and 99% can be achieved using conventional and DLE techniques. The low lithium concentration and high Mg/Li ratio in various hot springs, as well as the required energy and related cost, emerge as general factors to be considered during the selection of the proper recovery technology. Generally, DLE techniques tend to overcome critical issues associated with traditional methods (i.e., water loss, land use, and brine generation), but at higher costs. DLE methods, such as the use of metal doping, ionic liquids, and membrane technologies, can represent viable solutions to reduce environmental risks while improving lithium extraction from hot springs. However, potential drawbacks to using DLE due to Mn-Tn dissolution, aggressive organic solvents, and chemical waste solutions should be taken into account for a sustainable and environmentally friendly extraction.

CRediT authorship contribution statement

Giuseppe Di Sotto: Writing – original draft, Visualization, Methodology, Data curation, Conceptualization. **Francesco Bianco:** Writing – review & editing, Validation, Supervision, Software, Conceptualization. **Matteo Fiorucci:** Writing – review & editing, Validation, Supervision, Conceptualization. **Marco Race:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Michele Saroli:** Writing – review & editing, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The authors are unable or have chosen not to specify which data has been used.

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