minerals

Review

Spodumene: The Lithium Market, Resources and Processes

Colin Dessemond [1], Francis Lajoie-Leroux [1], Gervais Soucy [1,*], Nicolas Laroche [2] and Jean-François Magnan [2]

[1] Département de génie chimique et de génie biotechnologique, Université de Sherbrooke, Sherbrooke, QC J1K 2R1, Canada; Colin.Dessemond@USherbrooke.ca (C.D.); Francis.Lajoie-Leroux@USherbrooke.ca (F.L.-L.)
[2] Nemaska Lithium Inc., Quebec, QC G1K 3X2, Canada; Nicolas.Laroche@nemaskalithium.com (N.L.); jean-francois.magnan@nemaskalithium.com (J.-F.M.)
* Correspondence: Gervais.Soucy@USherbrooke.ca; Tel.: +1-819-821-8000 (ext: 62167)

Received: 17 April 2019; Accepted: 24 May 2019; Published: 29 May 2019

Abstract: This literature review gives an overview of the lithium industry, including the lithium market, global resources, and processes of lithium compounds production. It focuses on the production of lithium compounds from spodumene minerals. Spodumene is one of the most critical minerals nowadays, due to its high lithium content and high rate of extraction. Lithium is one of the most sought-after metals, due to the ever-growing demand for lithium-ion batteries (LiBs). The data on lithium extraction from minerals is scattered through years of patents, journal articles, and proceedings; hence, requiring an in-depth review, including the comprehension of the spodumene phase system, the phase conversion processes, and the lithium extraction processes.

Keywords: lithium review; spodumene processes; thermodynamic of spodumene; lithium extraction

1. Introduction

Lithium is the third element of the periodic table. It is the lightest of all solid elements (d = 0.53 g·cm^{-3} at 20 °C), has the highest specific heat capacity, the smallest ionic radius of all the alkali metals, and a high electrochemical potential [1]. Its two stable isotopes are ^{6}Li and ^{7}Li, with ^{7}Li being the most abundant (92.5%) [2,3]. Several radioisotopes have been observed, such as ^{3}Li, ^{4}Li, ^{5}Li, ^{8}Li, ^{9}Li, ^{10}Li, ^{11}Li, ^{12}Li, ^{13}Li [4], with ^{8}Li and ^{9}Li being the most stable, with a half-life of, respectively, 838 ms and 178 ms [5]. Lithium also contradicts the Big Bang Nucleosynthesis theory, which predicts the abundance of D, ^{3}He, ^{4}He, and ^{7}Li in the universe [6–8], with observed rates three times lower than predicted. This contradiction has apparently been solved [9].

Lithium is one of the most critical metals in modern industry. Its usages range from pharmacy with lithium-based bipolar disorder treatment drugs to aeronautics with light aluminum/lithium alloys. The most important usage nowadays is Lithium-ion Batteries (LiBs). The lithium production was, until recently, dominated by the salt lake brines, because of their cheaper production cost. The ever-growing demand in lithium compounds led to the regaining of interest for another source, after the lithium price increased. This other source, lithium rich minerals, now account for 50% of the world's lithium production [10]. Lithium minerals are numerous and include spodumene, eucryptite, petalite, bikitaite, etc. [11]. Lithium reserves estimations have significantly changed over the years, due to continuous exploration. Estimations have ranged from 16.7 Mt Li in minerals for a total of 43,6 Mt Li including the brines [12] to 14 Mt Li in minerals for a total of 62 Mt Li identified resources [13]. Among those minerals, spodumene $LiAlSi_2O_6$ is the most common and the most studied. It offers a theoretical Li_2O content of 8 wt %, whereas raw minerals in nature typically offer 1 to 2 wt % Li_2O with some notable exceptions such as Greenbushes, Australia which offers a high rate of 1,44 wt % Li (3.10 wt % Li_2O) [14]. This review will offer an overview of the lithium market, the sources of lithium, and the production processes, and will then focus on the chemical system of the spodumene, of the conversion methods and finally the extraction methods.

2. Lithium Usage and Resources

2.1. Usage

Lithium usages are wide. They range from glass and ceramics to pharmacy (Figure 1). Glass and ceramics were the main usage of lithium up to 2005 [15]. Since this date, Lithium ion Batteries (LiBs) have taken over, since they play a major role in the development of the electronic and green industries.

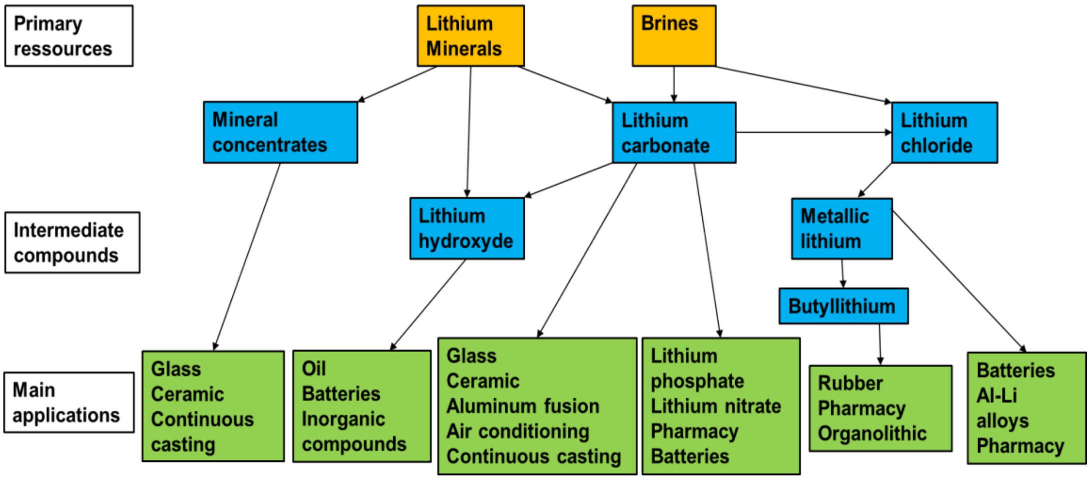


Figure 1. Diagram of lithium usages [16] (adapted with permission from Elsevier, Resources Policy; published by Elsevier, 2019).

Among those uses, LiBs show the highest growth rate and are expected to take an even bigger part in the lithium industry (Figure 2). The expected growth rate for lithium carbonate and lithium hydroxide is respectively 10% and 14.5% until 2025 [17], since they are two of the raw materials used for LiBs. In 2016, lithium carbonate prices were reported to range from 10,000 US$ to 16,000 US$ while lithium hydroxide prices were reported to range from 14,000 US$ to 20,000 US$ [18].

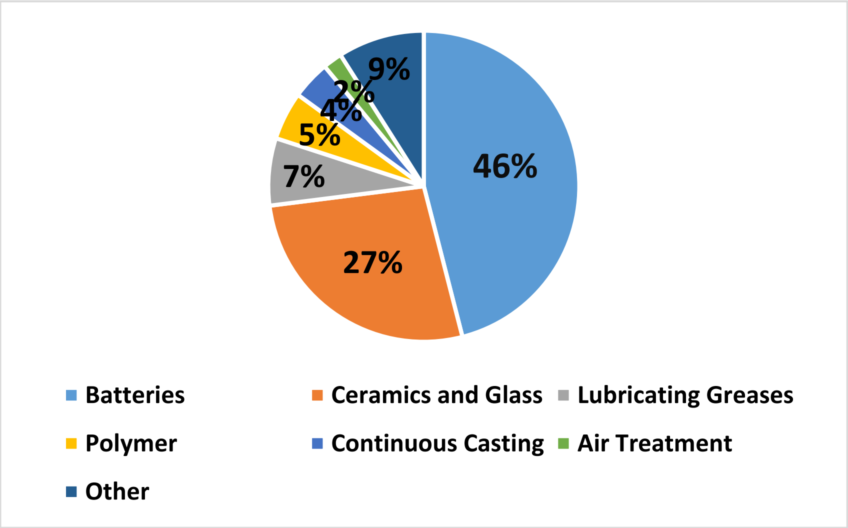


Figure 2. Diagram of lithium usage proportions [19].

When it comes to ceramics, lithium is used in its mineral forms, such as spodumene, to give economic and environmental benefits by reducing the melting temperature. Concerning the LiBs, lithium is used to manufacture cathodes, anodes, and electrolytes alike. Lithium greases are used for their excellent temperature properties (they are stable at a high temperature and do not solidify at a low temperature). Lithium bromide solutions play an important role in air treatment, and lithium hydroxide is used as CO_2 scrubbers in space shuttles and submarines.

2.2. Resources

The resources of lithium are primarily divided into three categories. The first are brines. They are, by far, the main source of lithium with more than 60% of the global identified reserves [12]. Among the brines, the salars, which are dried salt lakes, hold 78% of the lithium brine reserves. The second source, by amount of lithium available, is pegmatites. Recent estimations evaluate pegmatites as 23% to 30% of the lithium identified reserves [13]. Lithium-rich pegmatites, despite being one of the main sources of lithium worldwide, are very rare in comparison to pegmatites as a whole [20], forming less than 0.1% of the family.

The lithium minerals containing lithium inside those pegmatites are numerous and their lithium content varies greatly (Table 1).

Table 1. Principal lithium-bearing minerals [11].

Mineral	Formula	Theoretical Li Content (%)
Spodumene	$LiAlSi_2O_6$	3.73
Petalite	$LiAlSi_4O_{10}$	2.27
Eucryptite	$LiAlSiO_4$	5.51
Bikitaite	$LiAlSi_2O_6.H_2O$	3.40
Lepidolite	$KLi_2AlSi_3O_{10}(OH,F)_2$	~3.84
Zinnwaldite	$KLiFeAl_2Si_3O_{10}(F,OH)_2$	1.59
Amblygonite	$(Li,Na)AlPO_4(OH,F)$	4.73
Montebrasite	$LiAl(PO_4)(OH)$	1 to 4
Lithiophylite	$LiMnPO_4$	4.43
Triphylite	$LiFePO_4$	4.40
Hectorite	$Na_{0,3}(Mg,Li)_3Si_4O_{10}(OH)_2$	~1.93
Jadarite	$LiNaAlSiB_2O_7(OH)$	2.85
Zabuyelite	Li_2CO_3	18.79
Elbaite	$Na(Li_{1,5}Al_{1,5})Al_6Si_6B_3O_{27}(OH)_4$	1.11

The third source represents less than 3% of the global lithium resources. They are made of Sediment-Hosted Deposits. They are made of hectorite deposits and jadarite deposits. So far, two hectorite deposits are known, which are in McDermitt, United States and Sonora, Mexico. Only one jadarite deposit has been discovered in Jadar, Serbia. The main producers of lithium from minerals are Australia (40 kt Li), Chile (14.2 kt Li), China (6.8 kt Li), and Argentina (5.7 kt Li) for a global production of 69 kt Li. The biggest reserves (minerals only) are located in Chile (8 Mt Li), Australia (2.7 Mt Li), Argentina (2 Mt Li), and China (1 Mt Li). Other countries have a significant amount of identified reserves, which have yet to be categorized. An example of such a country is Canada, which has an identified reserve of 2 Mt Li [13]. The consumption of lithium by the electrical vehicle (EVs) industry is expected to reach 565 kt LCE (Lithium Carbonate Equivalent) or 106 kt Li by 2027 [21]. This would mean that minerals could provide the EVs industry for more than 130 years at maximum consumption (not accounting for the other lithium applications).

3. The Different Spodumene Phases

3.1. The Pegmatite Formation

Pegmatite is the name of a large family, which includes lithium aluminosilicates, among others. Pegmatites are divided between granitic and non-granitic pegmatites [22]. Spodumene is a granitic pegmatite [23–25]. Being very different in their nature, pegmatites forming a pluton are called a group.

Groups of pegmatite have a common granitic source, but differ from each other due to the nature of the source, depth, etc. [26,27]. In a perfect case, a group of pegmatite follows a regionally layered structure (Figure 3).

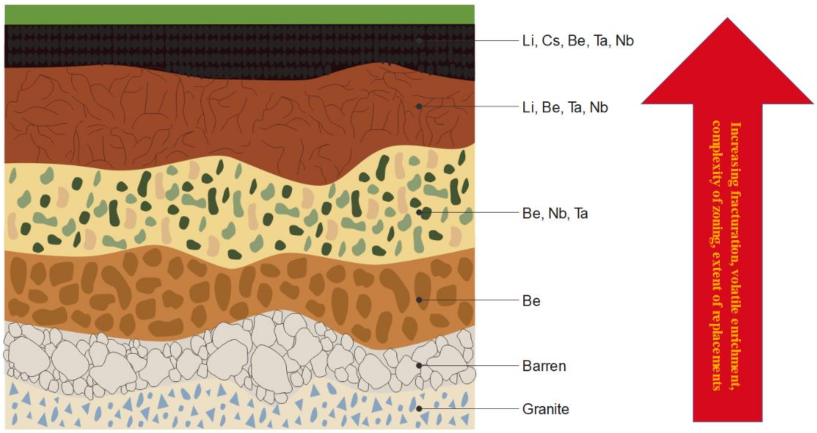


Figure 3. Chemical evolution through a lithium-rich pegmatite group with distance from the granitic source [28] (adapted with permission from the Mineralogical Association of Canada, Granitic Pegmatites in Science and Industry; published by the Mineralogical Association of Canada, 2019).

In the case of spodumene, a relation between its phases and other lithium aluminosilicates, such as eucryptite or petalite, exists in a quartz-saturated environment (Figure 4). This relationship between α-spodumene, β-spodumene and γ-spodumene (virgilite) shows that the crystallization of the minerals must have occurred under about 700 °C since β-spodumene does not occur naturally and virgilite is very rare and mostly found as inclusions [29].

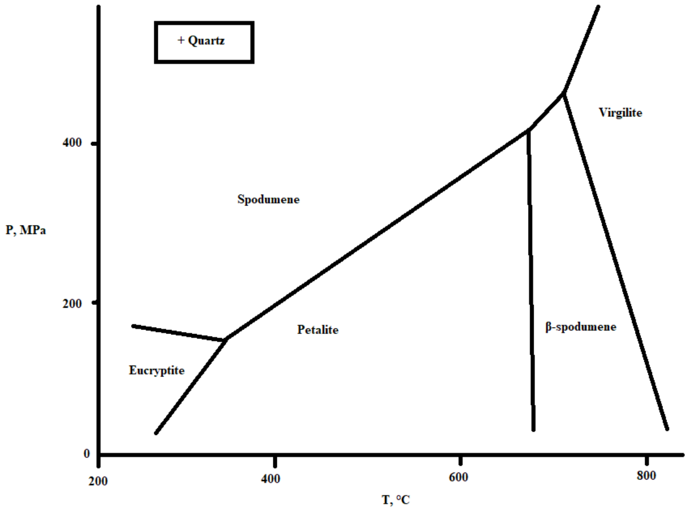


Figure 4. Stability relations among eucryptite ($LiAlSiO_4$), α-spodumene ($LiAlSi_2O_6$), petalite ($LiAlSi_4O_{10}$), β-spodumene ($LiAlSi_5O_{12}$) and virgilite ($LiAlSi_5O_{12}$), in the system $LiAlSiO_4$–SiO_2–H_2O [30] (adapted with permission from the Mineralogical Society of America, American Mineralogist; published by the Mineralogical Society of America, 2019).

3.2. The α, β, γ System

Spodumene is an aluminosilicate of lithium. It has been described for the first time in 1800 for an occurrence in Üto, Sweden [31]. Its name is derived from ancient Greek spodumenos, which means "burnt to ashes", due to its grey ash-like color when grinded. Its color ranges from green to purple. Spodumene can produce two kinds of gems, hiddenite (green), and kunzite (purple) [32]. The mineral is mostly associated with quartz and albite, with sometimes traces of beryl [33]. Geologists only call it spodumene. However, in the lithium industry, the mined natural material is referred to as α-spodumene. Its chemical formula is $LiAlSi_2O_6$ and it has a monoclinic structure and a density of 3.184 g·cm^{-3}. Its aspect and X-Ray pattern are presented below (Figures 5 and 6).

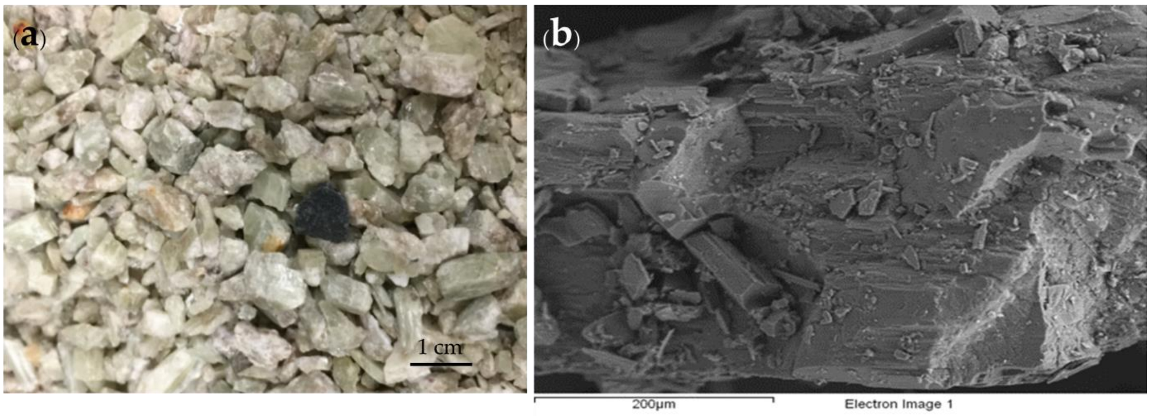


Figure 5. (**a**) Macroscopic (Optical), (**b**) Microscopic (SEM) aspects of a typical α-spodumene sample.

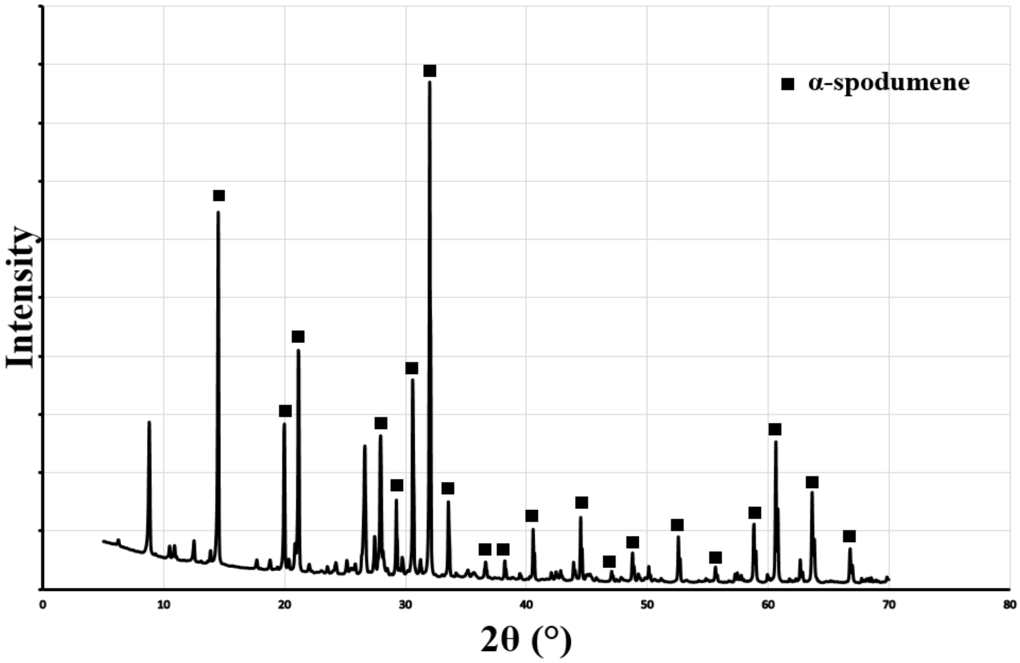
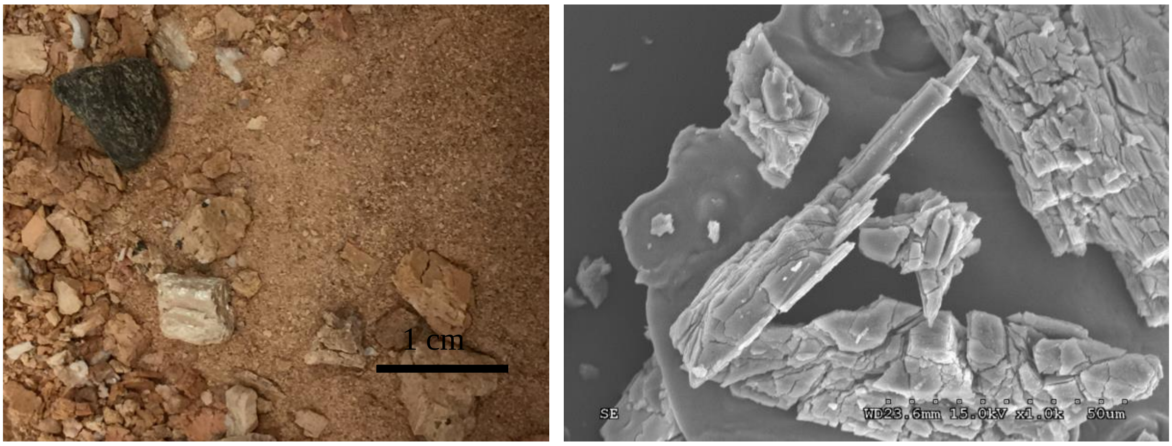


Figure 6. X-Ray pattern of a typical α-spodumene sample, only the main peaks of α-spodumene are indicated.

The second phase is called β-spodumene or spodumene-II. It is the most known phase of the system, due to its reactivity towards extraction. It is obtained after high temperature treatment of α-spodumene and is the base mineral of almost every lithium extraction processes. It has a tetragonal structure [34,35] and a density of 2.374 g·cm^{-3}. It has the particularity to be present in the

Li_2O–Al_2O_3–SiO_2 ternary equilibrium system. Therefore, it is possible to synthesize it directly into this form following, for example, the $LiAlO_2 + Al_6Si_2O_{13} = 3Al_2O_3 + \beta\text{-}LiAlSi_2O_6$ reaction [36].

The third phase is less known and has several different names. It is referred to as virgilite, γ-spodumene or spodumene-III [37,38]. It has a hexagonal structure and a density of 2.399 $g{\cdot}cm^{-3}$. The formation of a pure γ-spodumene sample has not been reported yet. Given that γ-spodumene is never pure, the aspects and X-Ray patterns of β-spodumene and γ-spodumene are presented together below (Figures 7–9). As seen on the X-Ray patterns, β-spodumene and γ-spodumene share the same angle for their main peak. Moreover, γ-spodumene's peaks are fewer in number and lower in intensity, making it difficult to identify γ-spodumene in a sample.



(**a**) (**b**)

Figure 7. (**a**) Macroscopic (Optical), (**b**) Microscopic (SEM) aspects of a typical β-spodumene sample (red-brown particles).

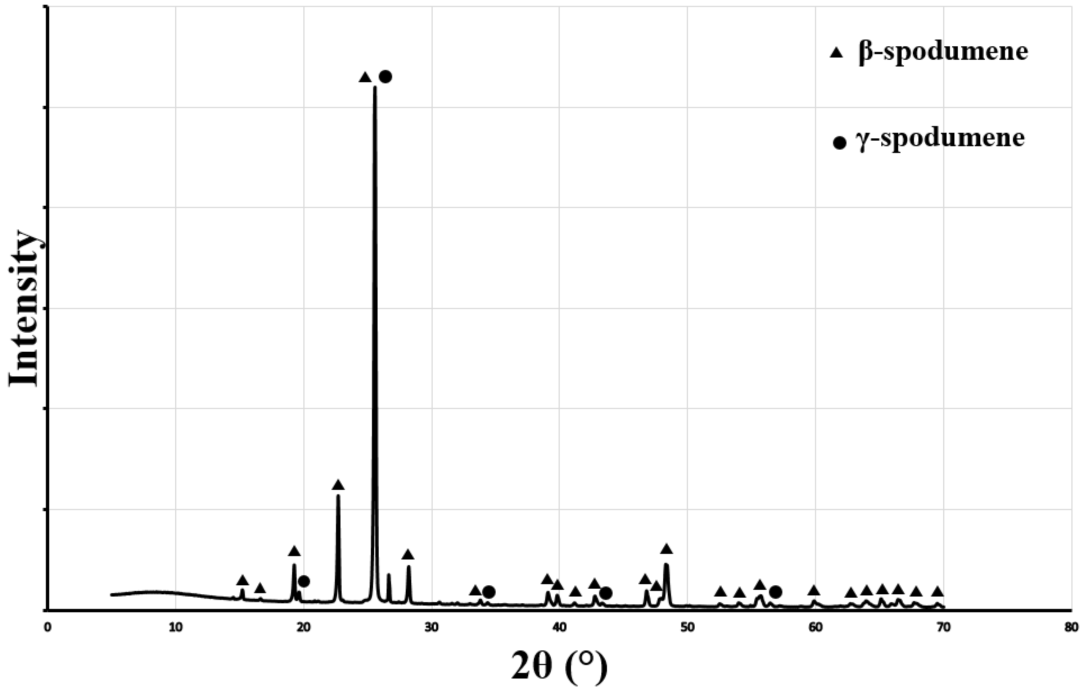


Figure 8. X-Ray pattern of a typical β-spodumene and γ-spodumene sample.

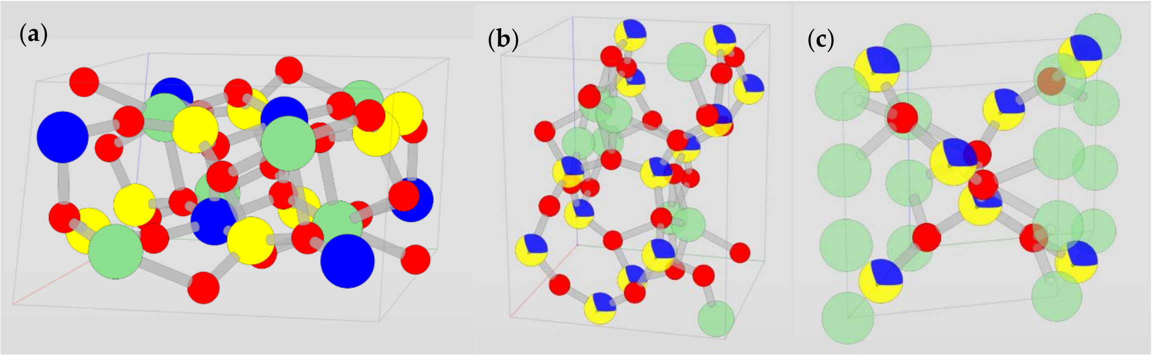


Figure 9. Crystal structures of spodumene. (**a**) α-spodumene, (**b**) β-spodumene, (**c**) γ-spodumene. Red: Oxygen. Yellow: Silicon. Blue: Aluminum. Green: Lithium. Note: The lattices images were obtained with the display module of the Jade2010^{TM} software. At a macroscopic level, α-spodumene appears as a very hard rock. It is compact and difficult to cut or grind while β-spodumene appears as a dusty material with a low resistance to grinding. At a microscopic level, α-spodumene appears as a compact material made out of multiple layers stacked on top of each other while β-spodumene presents many cracks on its particles, which make its structure more random.

The space groups and crystallographic data of the three phases are listed in the table below (Table 2 and Figure 9).

Table 2. Crystallographic data of the different spodumene structures [34,38,39].

Form	Structure	Space Group	*a* (Å)	*b* (Å)	*c* (Å)	Angles (°)	*Z*
α-spodumene	Monoclinic	$C2/c$	9.45	8.39	5.215	$\beta = 110$	4
β-spodumene	Tetragonal	$P4_32_12$	7.541	-	9.156	-	4
γ-spodumene	Hexagonal	$P6_222$	5.217	-	5.464	-	1

The thermodynamic data of the three phases have been measured and are listed below (Table 3).

Table 3. Data of the different spodumene phases [40,41] (adapted with permission from Springer Nature, Contributions to Mineralogy and Petrology; published by Springer Nature, 2019).

Form	C_p(298 K) (J·K^{-1}·mol^{-1})	$H^0{}_i$ (kJ·mol^{-1})	$S^0{}_i$ (J·K^{-1}·mol^{-1})
α-spodumene	158.93	−3053.500	129.412
β-spodumene	162.77	−3031.888	155.376
γ-spodumene	162.77	−3032.128	162.038

When it comes to the C_p of the three phases, their relations to temperature have been calculated [40].

α-spodumene:

$$C_p(T) = 354.715 - 3375.72\, T^{-0.5}\, J.mol^{-1}.K^{-1} \tag{1}$$

β-spodumene and γ-spodumene:

$$C_p(T) = 362.8 - 0.003684\, T - 3435.0\, T^{-0.5}\, J.mol^{-1}.K^{-1} \tag{2}$$

The phase transitions occur during the thermal treatment via a phenomenon called decrepitation. The latter is an expansion of the crystal lattice of the compound after reaching a determined temperature. The α-spodumene to β-spodumene transition occurs above 950 °C [42] and is endothermic [43]. The crystal lattice expands massively (27%) during the phase transition [44]. The γ-spodumene is known to appear before the β-spodumene [37] but is metastable and transitions to β-spodumene at higher temperatures.

The transitions existing within the spodumene system can be summarized as follows (Figure 10). Every single transition is irreversible.

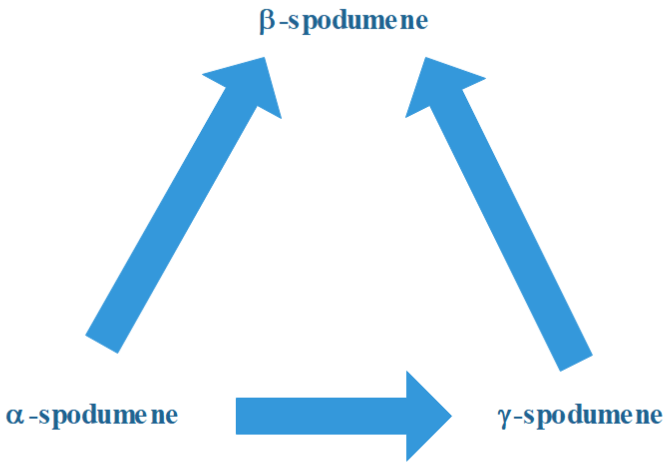


Figure 10. Transitions occurring at high temperature (above 900 °C) in the spodumene system.

3.3. General Flow Sheets

The lithium compounds production from minerals follows a simple succession of steps. Every raw mineral has to be grinded before being cleaned. A heat treatment is then applied before roasting. The process allows the recovery of lithium but not the production of technical lithium hydroxide of lithium carbonate. Another step, such as carbonation or electrodialysis is needed (Figure 11).

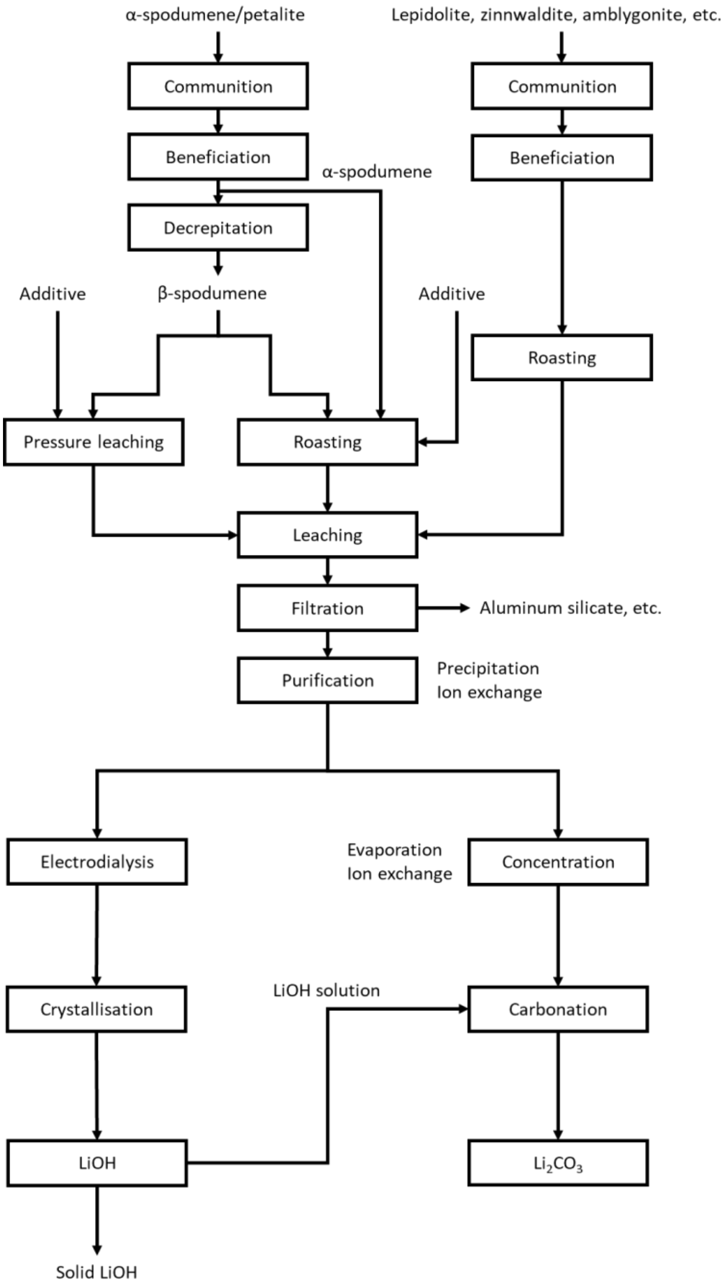


Figure 11. Flow sheets for the production of lithium compounds from mineral sources. Few steps, such as electrodialysis, have only been tested in feasibility studies [45] (adapted with permission from Elsevier Books, Lithium Process Chemistry; published by Elsevier, 2019).

Concerning the lithium production from brines, the process revolves around concentrating the brines up to 6 wt% Li and removing the impurities one after the other (Figure 12). There has been research on the efficiency of lithium extraction, both ancient and novel. For example, fluorinated β-diketones have been investigated to separate lithium from sodium, potassium, rubidium, and caesium, due to their poor selectivity for lithium [46]. More recently, N-butyl pyridinium bis[(trifluoromethyl)sulfonyl]imide solution was found to have a high efficiency for lithium extraction from brines [47]. Other processes involving, for example, LiAl-layered double hydroxides as lithium-ion-selective capturing material, were proven to have lithium yields over 96% [48].

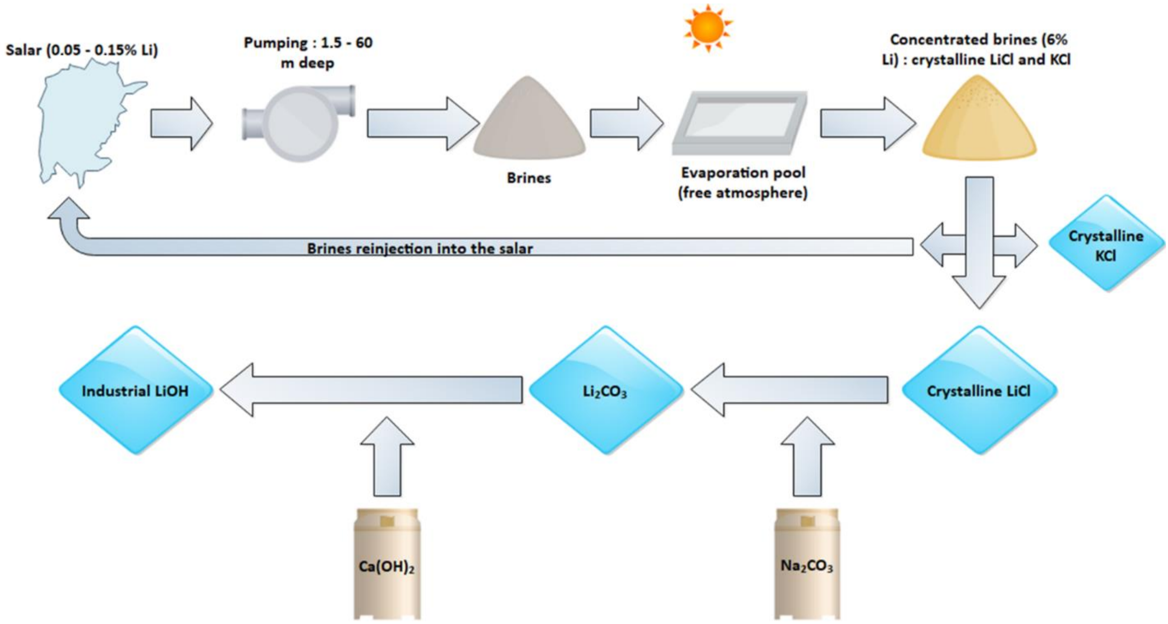


Figure 12. Flow sheets for production of lithium compounds from brines.

4. Production of Lithium from Spodumene

4.1. The Traditional Process

When it comes to the actual phase conversion of spodumene, the process has been known since the 1950s. The process has been patented [49] and, still nowadays, heavily dominates the lithium production industry. This process starts with the crushing of spodumene ore. The cause behind the grinding of the spodumene is an acceleration of the heat transfer between the surrounding atmosphere and the mineral. The crushed mineral is then heated in a furnace at, at least, 1000 °C for 30 min. It is stated that almost any kind of furnace will do for this part of the process. The thermal treatment will allow the α-spodumene to decrepitate into β-spodumene. However, nowhere in this process is it stated that γ-spodumene exists. Therefore, the data concerning the spodumene phase transitions is not complete. This process is stated to be exclusive to spodumene. The other lithium-bearing minerals being impossible to decrepitate using this method. It was the first process to efficiently extract lithium from spodumene (85% to 90% lithium yield at the time) and was scaled up shortly after [50]. The lithium extraction went from total digestion of minerals such as lepidolite ($K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$) or amblygonite ($(Li,Na)AlPO_4(F,OH)$) followed by complex purification to selective extraction of lithium.

The process is based on the higher reactivity of β-spodumene towards sulphuric acid. The acid is brought into contact with the β-spodumene and heated at about 250 °C. It is reported that the temperature can go as low as 200 °C but cannot reach higher than 300 °C, temperature at which the sulphuric acid starts to decompose. The acid excess must be at least 30% to ensure the availability of the protons after reactions with impurities such as potassium or sodium. Depending on the grade of the ore, acid excess can go up to 140%. The reaction between the sulphuric acid and the spodumene is presented below.

$$2\,LiAlSi_2O_6\ (s) +\ H_2SO_4\ (l)\ \rightarrow 2\,HAlSi_2O_6\ (s) + Li_2SO_4(s) \tag{3}$$

After reaction between the acid and the concentrate, the lithium sulphate is leached by water in which it dissolved while leaving the leached concentrate in its solid state. The lithium sulphate can thereafter be precipitated as is, or transformed into lithium chloride or lithium carbonate.

The authors of this patent have come to three statements, all of them being in favor of a diffusion mechanism allowing the protons to diffuse through the β-spodumene to allow the cationic exchange.

1. α-spodumene is almost completely resilient toward acid roasting contrary to β-spodumene
2. β-spodumene density is significantly lower than that of α-spodumene.
3. The structure of the leached β-spodumene is very similar to that of β-spodumene.

Hence, β-spodumene has a more open structure. This structure would allow the diffusion of ions through its matrix via a pseudo-Brownian movement. This statement was later confirmed by crystallographic studies [51] which confirmed that the structure of β-spodumene presents pseudo-zeolithic channels in which protons and lithium cations are free to move. The aluminosilicate portion of β-spodumene is in fact isostructural to keatite, which presents those channels. An important heat production is observed during the acid roasting around 175 °C. This exothermic reaction is linked to the formation of liquid lithium bisulfate ($LiHSO_4$) as a reaction intermediate [52,53] since it has a melting point of around 170 °C.

This process was so efficient and easy to implement that it has been considered the one and only method of extracting lithium from spodumene in the lithium industry. From there, two major steps can be pointed out. The first one is the lithium extraction from β-spodumene and the second is the decrepitation of α-spodumene.

4.2. Other Processes of Extracting Lithium from Spodumene

The lithium extraction from β-spodumene has always been considered the critical step of the overhaul process and the one where major improvements on the lithium yield could be made. Therefore, this step has been heavily researched and still is nowadays. From the middle of the 20th century until the late 1960s, several processes concerning the extraction of lithium from spodumene have been patented. Those patents are listed below (Table 4). Only the processes involving H_2SO_4 (l), or a mixture of $CaCO_3$ (s) + $CaSO_4$ (s), have been commercially exploited, the others having been dismissed due to low lithium yield, high temperature or long duration.

Table 4. Patented processes of lithium extraction from spodumene [54].

Reagent(s)	Size (µm)	Yield (%)	Decrepitation (°C)	Temperature (°C)	Duration	Reference
H_2SO_4 (l)	<600	90	1000	250	« Short »	[49]
$Ca(OH)_2$ (aq.)	<100	90	1100	100–205	2 h	[55]
$CaCO_3$ (s) + $CaSO_4$ (s)	<75	85–90	-	During the decrepitation		[56]
CaO (s)	-	84–100	-	700	-	[57]
$CaCO_3$ (s) + $CaCl_2$ (s) + SiO_2 (s)	<175	90–95	900–1100	1100–1200	-	[58]
$(NH_4)_2SO_4/NH_4HSO_4$ (l)	<175	-	1030	150–370	-	[59]
KCl (s) + KCl·NaCl (s)	<150	100	1050	During the decrepitation		[60]
NaCOOH + Na_2CO_3	<300	98–100	100	290	30–90 min	[61]
SO_3 (g)	<600	97	870	335–450	15 min	[52]
$NaOH/Na_2CO_3$ (aq.) + $CaO/Ca(OH)_2$ (aq.)	-	-	1010	100–200	-	[62]
$NaOH/Na_2SiO_3/2Na_2O{\cdot}B_2O_3/Na_2S$ (aq.)	<150	93	-	70–130	1–48 h	[63]
Na_2CO_3 (s)	-	85–97	1000	450–750	10–120 min	[64]
Cl_2 (g) + CO (g)	<44	90	1040	1000	-	[65]

Despite the domination of the traditional process [49], some research on alternative processes have been published (Table 5). None of those new processes has been commercially exploited, mainly because of the reticence of the companies to deviate from the long-established process.

Table 5. Published processes of lithium extraction from spodumene [54].

Reagent(s)	**Size (µm)**	**Yield (%)**	**Decrepitation (°C)**	**Temperature (°C)**	**Duration**	**Reference**
$CaMg_2Cl_6{\cdot}12H_2O$ (s)	<75	87	1100	During the decrepitation		[66]
Mg(l)	-	100	1050	1500	-	[67]
Bacteria (aq.)	-	<10	No decrepitation	Room	30 d	[68]
Na_2CO_3 (aq.)	-	94	1050	225	1 h	[69]
Na_2CO_3 (s)/H_2O/H_2O + NH_4HCO_3 (aq.)	-	<10	-	600 then room	30 min then 4 h	[70]
HF (aq)	-	90	1100	75	20 min	[71]
Cl_2 (g)	<50	99	1180	1000	3 h	[72]
$CaCl_2$ (s)	<50	90	1180	900	2 h	[73]
Na_2SO_4 (aq)/NaOH or CaO (aq.)	<75	90	1100	230	-	[74]

A few things can be pointed out when it comes to the extraction of lithium from spodumene. First, γ-spodumene is ignored or even not reported in those studies, which means that its reactivity towards reagents is unknown. Therefore, its influence on the lithium yields is unknown. Second, there is no consistency concerning the granulometry of the samples used. Therefore, the influence of granulometry on the lithium yield cannot be evaluated. Those should not be underestimated because of the high cost related to communition [75] and the wasteful nature of communition [76]. Last, there is no consistency about the decrepitation temperature, while this temperature is known to have an effect on spodumene conversion and thus on lithium extraction.

When it comes to the impurities of spodumene and their influence on lithium extraction, research is scarce. However, it was pointed out that impurities were leached at rates independent of leaching conditions [77]. On the other hand, it was found out that quartz particles could protect β-spodumene particles from the sulphuric acid by coating them (Figure 13).

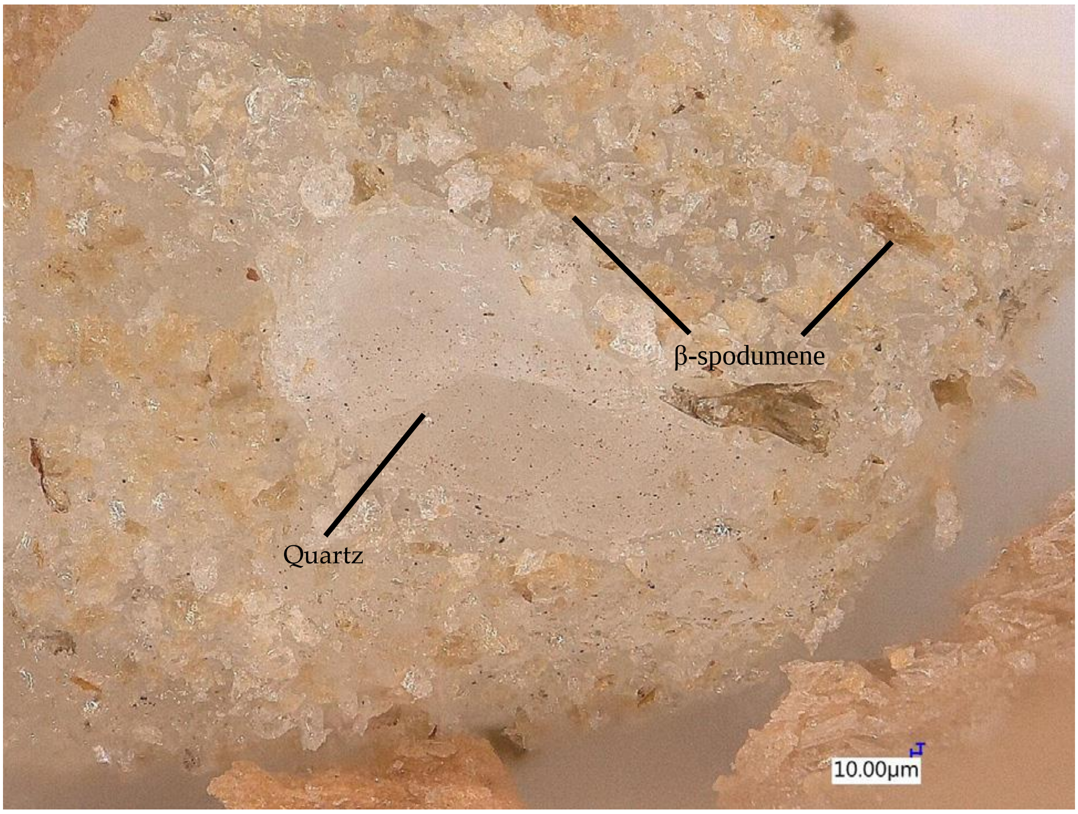


Figure 13. β-spodumene particles included within a quartz matrix. The big white and translucent particle is quartz and the smaller orange particles contained inside are mostly spodumene [77] (reproduced with permission from Elsevier, Minerals Engineering; published by Elsevier, 2019).

4.3. Conversion Processes of Spodumene

As stated in Section 3.2, the critical step of the process has always been considered to be the extraction step. Since the beginning of the selective extraction of lithium, decrepitation has been considered a minor step of the process where only minor improvements could be made. Hence, there is very little data on the behavior of spodumene with regards to the granulometry of the sample, the temperature of decrepitation, etc. There has been very little research on how to improve the decrepitation step of spodumene, many considering that the furnace heating in a rotary kiln is optimized. An equation describing the conversion of spodumene was derived from the Avrami equation [78] and is presented below.

$$1 - \omega = exp(-Kt) \tag{4}$$

Where ω is the converted spodumene, K the rate of conversion and t the treatment time. This equation was developed from the Avrami equation and is considered an approximation of the phase transition, since the kinetic model only considers one molecule. The results presented by this study suggest that above 950 °C, the phase transition is almost instantaneous. The downside is that it does not consider the γ-spodumene. A compilation of spodumene studies shows that the decrepitation temperature differs greatly between the samples [79], with temperatures ranging from 950 to 1050 °C. Moreover, it was found that the temperature range suitable for the decrepitation becomes narrower with the increasing amount of impurities [80]. This was further later confirmed using the Delmon theory. According to this theory, the activation energy of the spodumene conversion is 296 kJ/mol ± 6 kJ/mol and is independent of the rate of impurities. This value fits the results found from the Avrami equation between 950 and 1050 °C. It was then concluded that the temperature of conversion was indeed influenced by the amount of impurities in the spodumene [43].

Despite the general consensus that the traditional method of decrepitating spodumene is the best, there has recently been some research about alternative methods to the rotary kiln. One still uses traditional heating but emphasizes on the grinding of the spodumene beforehand. It is stated that grinding cleaves the Li–O, Al–O, and Si–O–Si bonds from the tetrahedral site. It shows that the α-spodumene turns into γ-spodumene between 700 and 900 °C before transitioning into β-spodumene between 900 and 950 °C [81]. This would mean a decrease in the energy necessary to decrepitate the spodumene but does not consider the amount of energy needed to grind the material. One of the few alternative processes uses microwaves to decrepitate spodumene ore. This study found that the critical temperature for α-spodumene to start absorbing microwaves is about 634 °C. But it also states that the temperature is not uniform, with measures ranging from 650 to 1250 °C depending on the area of measurement. A significant amount of β-spodumene melts using this method, while the intermediate layer is composed of β-spodumene and γ-spodumene and the top layer is still in α-form [82]. Hybrid microwaving has also been studied using SiC susceptor tubes. It can allow the decrepitation to occur, despite a higher temperature of 1197 °C. The upside of this method is a shorter treatment time of only 170 s [37]. It also shows that γ-spodumene is formed if the temperature is not high enough and that this method also melts the concentrate. When it comes to the melting of the samples, it has been reported that the behavior of a spodumene sample differs greatly based on the impurities in the sample and their quantity [83], with melting temperatures ranging from 1000 to 1400 °C. For example, the melting point of the spodumene can go down as low as 930 °C if the sample is made of 50/50 α-spodumene/(Quartz–Albite–Microcline 10–20–20) [84].

If the decrepitation of the spodumene was studied, the effect of the phenomena on the size of the particle is not mentioned. It has been proven that decrepitation was able to grind coarse particles (size ranging from 2 mm to 2 cm) into micrometric particles suitable for acid roasting. This study shows that heating a coarse spodumene concentrate at 1050 °C for 30 min decrepitates the α-spodumene into β-spodumene and γ-spodumene with 65% of the initial mass becoming smaller than 180 μm and that some impurities were not affected by the thermal treatment, making them easy to remove from the converted concentrate. This study was realized without prior grinding or flotation of the mineral and found out that the lithium in the finer fraction was being extracted at a 99% yield using the traditional method [85], meaning that the need for grinding and flotation could be reduced, thus saving time and energy.

As can be seen above, when it comes to research about the decrepitation of the spodumene, γ-spodumene is taken into account in the recent studies while this is not the case with lithium extraction and older decrepitation studies. This shows that despite the disappearance of α-spodumene, the conversion of spodumene does not give only β-spodumene. It could mean that the limitations may not have originated only from the sulphuric acid behavior toward β-spodumene but also from the behavior of γ-spodumene itself.

5. Conclusions

Lithium is one of the most sought after metals in the modern industry. Spodumene is one of the most important sources of lithium in minerals. Many lithium companies use spodumene as their primary source and transform it into lithium using a process that was first introduced in 1950 and little improved over the years. As seen in this review, the literature concerning the thermal treatment is not complete. While finding new processes to decrepitate spodumene may not be necessary, it would be necessary to include γ-spodumene in every work to research its influence on the whole process. The granulometry of the samples and their grade should be mentioned since this seems to have great influence over the behavior of spodumene and ultimately on lithium yield. On the contrary, the process of extraction in itself has been heavily studied to try to give reasons for the limitations of the traditional process. Alternatives to the sulphuric acid process have been studied but little to none have been commercially exploited due to the reticence of the companies to deviate from a reliable and relatively efficient process.

Author Contributions: Writing—original draft preparation, C.D.; writing—review and editing, G.S., F.L.-L., N.L., J.F.-M.; supervision, G.S.

Funding: The research was funded by Fonds de recherche Nature et technologies, grant number 2015-MI-192454 and by Nemaska Lithium inc. with a mandatory portion of funding requested by the government funder.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Christmann, P.; Gloaguen, E.; Labbé, J.F.; Melleton, J.; Piantone, P. Global lithium resources and sustainability issues. In *Lithium Process Chemistry*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 1–40.
2. Coplen, B.; Böhlke, J.K.; De Bièvre, P.; Ding, T.; Holden, N.E.; Hopple, J.A.; Krouse, H.R.; Lamberty, A.; Peiser, H.S.; Revesz, K.; et al. Isotope-abundance variations of selected elements (IUPAC Technical Report). *Pure Appl. Chem.* **2002**, *74*, 1987–2017. [CrossRef]
3. Tomascak, P.B. Developments in the Understanding and Application of Lithium Isotopes in the Earth and Planetary Sciences. *Rev. Mineral. Geochem.* **2004**, *55*, 153–195. [CrossRef]
4. Audi, G.; Kondev, F.G.; Wang, M.; Pfeiffer, B.; Sun, X.; Blachot, J.; MacCormick, M. The NUBASE2012 evaluation of nuclear properties. *Chin. Phys. C* **2012**, *36*, 1157–1286. [CrossRef]
5. Audi, G.; Bersillon, O.; Blachot, J.; Wapstra, A.H. The Nubase evaluation of nuclear and decay properties. *Nuc. Phys. A* **2003**, *729*, 3–128. [CrossRef]
6. Cyburt, R.H.; Fields, B.D.; Olive, K.A. Primordial nucleosynthesis in light of WMAP. *Phys. Lett. B* **2003**, *567*, 227–237. [CrossRef]
7. Coc, A.; Vangioni-Flam, E.; Descouvemont, P.; Adahchour, A.; Angulo, C. Updated big bang nucleosynthesis compared with wilkinson microwave anisotropic probe observations and the abundance of light elements. *Am. Astron. Soc.* **2004**, *600*, 544–552.
8. Asplund, M.; Lambert, D.L.; Nissen, P.E.; Primas, F.; Smith, V.V. Lithium isotopic abundances in metal-poor halo stars. *Am. Astron. Soc.* **2006**, *644*, 229–259. [CrossRef]

9. Hou, S.Q.; He, J.J.; Parikh, A.; Kahl, D.; Bertulani, C.A.; Kajino, T.; Mathews, G.J.; Zhao, G. Non-extensive statistics to the cosmological lithium problem. *Astrophys. J.* **2017**, *834*, 165–170. [CrossRef]
10. U.S. Geological Survey. *Mineral commodity summaries 2016: U.S. Geological Survey Lithium*; USGS: Reston, VA, USA, 2016; p. 202.
11. Labbé, J.F.; Daw, G. *Panorama 2011 du marché du lithium*; Rapport public 2012, BRGM/RP-61340-FR; BRGM: Orléans, France, 2012; p. 94.
12. Grosjean, C.; Miranda, P.H.; Perrin, M.; Poggi, P. Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry. *Renew. Sustain. Energy Rev.* **2012**, *166*, 1735–1744. [CrossRef]
13. Jaskula, B.W. Lithium. In *Mineral Commodity Summaries 2019*; USGS: Reston, VA, USA, 2019; pp. 98–99.
14. Kesler, S.E.; Gruber., P.W.; Medina., P.A.; Keoleian., G.A.; Everson., M.P.; Wallington., T.J. Global lithium resources: Relative importance of pegmatite, brine and other deposits. *Ore Geol. Rev.* **2012**, *48*, 55–69. [CrossRef]
15. *Sociedad Quimica y Minera de Chile, 2003 to 2013, Annual Reports*; SQM: Santiago, Chile, 2003–2013.
16. Yaksic, A.; Tilton, J.E. Using the cumulative availability curve to assess the threat of mineral depletion: The case of lithium. *Resour. Policy* **2009**, *34*, 185–194. [CrossRef]
17. SignumBOX. *Analysis: Lithium, Batteries and Vehicles/Perspectives and Trends*; SignumBOX: Santiago, Chile, 2014; p. 8.
18. Jaskula, B.W. *Lithium, 2016 Mineral Yearbook 2018*; USGS: Reston, VA, USA, 2018; p. 44.1.
19. Jaskula, B.W. *Lithium, Mineral Commodity Summaries 2018*; USGS: Reston, VA, USA, 2018; p. 1.
20. Laznicka, P. *Giant Metallic Deposits*; Springer: Berlin, Germany, 2006.
21. *Lithium-ion Batteries Market Development & Raw Materials*; Roskill: London, England, 2018.
22. Jahns, R.H.; Tuttle, O.F. *Layered Pegmatite-Aplite Intrusives*; Mineralogical Society of America: Chantilly, VA, USA, 1963; pp. 78–92.
23. Swanson, S.E. Mineralogy of Spodumene Pegmatites and Related Rocks in the Tin-Spodumene Belt of North Carolina and South Carolina, USA. *Can. Mineral.* **2012**, *50*, 1589–1608. [CrossRef]
24. Stewart, D.B. Petrogenesis of lithium-rich pegmatites. *Am. Mineral.* **1978**, *63*, 970–980.
25. Barros, R.; Menuge, J.F. The Origin of Spodumene Pegmatites Associated with the Leinster Granite in Southeast Ireland. *Can. Mineral.* **2016**, *54*, 847–862. [CrossRef]
26. Černý, P.; Ercit, T.S. The classification of granitic pegmatites revisited. *Can. Mineral.* **2005**, *43*, 2005–2026. [CrossRef]
27. London, D. Pegmatites. *Can. Mineral.* **2008**, *10*, 18.
28. Trueman, D.L.; Černý, P. Exploration for rare-element granitic pegmatites. In *Short Course Granitic Pegmatites in Science and Industry*; Mineralogical Association of Canada: Québec, QC, Canada, 1982; Volume 8, pp. 463–494.
29. French, B.M.; Jezek, P.A.; Appleman, D.E. Virgilite, a new lithium aluminum silicate mineral from the Macusani glass, Peru. *Am. Mineral.* **1978**, *63*, 461–465.
30. London, D. Experimental phase equilibria in the system $LiAlSiO_4$-SiO_2-H_2O: A petrogenetic grid for lithium-rich pegmatites. *Am. Mineral.* **1984**, *69*, 995–1004.
31. d'Andrada, J.B. Der eigenschaften und kennzeichen einiger neuen fossilien aus Schweden und Norwegen nebst einigen chemischen bemerkungen ueber dieselben. *Allgemeines J. Chem.* **1800**, *4*, 28–39.
32. Sthulman, O. The thermophosphorescent radiations of Hidennite and Kunzite. *J. Opt. Soc. Am. Rev. Sci. Instrum.* **1929**, *18*, 365–369. [CrossRef]
33. Anthony, J.W.; Bideaux, R.A.; Bladh, K.W.; Nichols, M.C. Spodumene. In *Handbook of Mineralogy*; Mineralogical Society of America: Chantilly, VA, USA, 2015. Available online: http://www.handbookofmineralogy.org/ (accessed on 12 March 2019).
34. Li, C.T.; Peacor, D.R. The crystal structure of $LiAlSi_2O_6$-II (β-spodumene). *Zeitschrift für Kristallographie* **1967**, *126*, 46–65. [CrossRef]
35. Keat, P.P. A new crystalline silica. *Science* **1954**, *120*, 328–330. [CrossRef]
36. Lu, H. Formation of β-Eucryptite and β-spodumene from Topaz Mixture. Ph.D Thesis, University of New South Wales, Sydney, Australia, 2005.
37. Peltosaari, O.; Tanskanen, P.A.; Heikkinen, E.P.; Fabritius, T. $\alpha \rightarrow \gamma \rightarrow \beta$-phase transformation of spodumene with hybrid microwave and conventional furnaces. *Miner. Eng.* **2015**, *82*, 54–60. [CrossRef]

38. Li, C.T. The crystal structure of $LiAlSi_2O_6$ III (high-quartz solid solution). *Zeitschrift für Kristallographie* **1967**, *127*, 327–334.
39. Anthony, J.W.; Bideaux, R.A.; Bladh, K.W.; Nichols, M.C. Virgilite. In *Handbook of Mineralogy*; Mineralogical Society of America: Chantilly, VA, USA, 2015. Available online: http://www.handbookofmineralogy.org/ (accessed on 12 March 2019).
40. Fasshauer, D.W.; Chatterjee, N.D.; Cemic, L. A thermodynamic analysis of the system $LiAlSiO_4$-$NaAlSiO_4$-Al_2O_3-SiO_2-H_2O based on new heat capacity, thermal expansion, and compressibility data for selected phases. *Contrib. Mineral. Petrol.* **1998**, *133*, 186–198. [CrossRef]
41. Robie, R.A.; Hemingway, B.S. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures*; USGS: Reston, VA, USA, 1995; Volume 2131, pp. 1–461.
42. Salakjani, N.K.; Singh, P.; Nikoloski, A.N. Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: Conventionnal heating. *Miner. Eng.* **2016**, *98*, 71–79. [CrossRef]
43. Botto, I.L.; Arazi, S.C.; Krenkel, T.G. Aplicación de la teoría de Delmon al estudio des mecanismo de la transformación polimórfica espodumeno I en espodumeno II. *Boletin Sociedad Española Cerámica Vidrio* **1976**, *15*, 5–10.
44. Brook, R.J. *Concise Encyclopedia of Advanced Ceramic Materials*; Pergamon Press: Oxford, England, 1991.
45. Tran, T.; Luong, V.T. Lithium production processes. In *Lithium Process Chemistry*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 81–124.
46. Seeley, F.G.; Baldwin, W.H. Extraction of lithium from neutral salt solutions with fluorinated β-diketones. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1049–1052. [CrossRef]
47. Wang, X.; Jing, Y.; Liu, H.; Yao, Y.; Shi, C.; Xiao, J.; Wang, S.; Jia, Y. Extraction of lithium from salt lake brines by bis[(trifluoromethyl)sulfonyl]imide-based ionic liquids. *Chem. Phys. Lett.* **2018**, *707*, 8–12. [CrossRef]
48. Sun, Y.; Guo, X.; Hu, S.; Xiang, X. Higly efficient extraction of lithium from salt lake brine by LiAl-layered double hydroxides as lithium-ion-selective capturing material. *J. Energy Chem.* **2019**, *34*, 80–87. [CrossRef]
49. Ellestad, R.B.; Leute, K.M. Method of extracting lithium values from spodumene ores. U.S. Patent 2,516,109, 25 July 1950.
50. Hader, R.N.; Nielsen, R.L.; Herre, M.G. Lithium and its compounds. *Ind. Eng. Chem.* **1951**, *43*, 2636–2646. [CrossRef]
51. Skinner, B.J.; Evans, H.T. β-spodumene solid solutions and the join Li_2O–Al_2O_3–SiO_2. *Am. J. Sci.* **1960**, *258-A*, 312–324.
52. Archambault, M.; Macewan, J.U.; Olivier, C.A. Method of producing lithium carbonate from spodumene. U.S. Patent 3,017,243, 16 January 1962.
53. Xiao, M.; Wang, S.; Zhang, Q.; Zhang, J. Leaching mechanism of the spodumene sulphuric acid process. *Rare Met. (Beijing)* **1997**, *16*, 36–44.
54. Lajoie-Leroux, F. *Étude sur le Grillage Acide du β-spodumene: Comportements des impuretés, Maîtrise*; Université de Sherbrooke: Sherbrooke, QC, Canada, 2018.
55. Clifford, M.N. Production of lithium compounds. U.S. Patent 2,413,644, 31 December 1946.
56. Hayes, E.T.; Sternberg, W.M.; Williams, F.P. Production of lithium chloride from spodumene. U.S. Patent 2,533,246, 12 December 1950.
57. Adolphe, V.K. Method of recovering lithium compounds from lithium minerals. U.S. Patent 2,662,809, 15 December 1953.
58. Cunningham, G.L. Preparation of lithium chloride from spodumene. U.S. Patent 2,627,452, 3 February 1953.
59. Dwyer, T.E. Recovery of lithium from spodumene ores. U.S. Patent 2,801,153, 30 July 1957.
60. Peterson, J.A.; Gloss, G.H. Lithium values recovery process. U.S. Patent 2,893,828, 7 July 1959.
61. Peterson, J.A. Process for recovering lithium values. U.S. Patent 2,924,507, 9 February 1960.
62. Chubb, P.A. Treatment of lithium ores. U.S. Patent 3,073,673, 15 January 1963.
63. Lemay, H.P.; Archambault, M.; Savard, M.A.O.C. Sodium-ammonium compounds process for extracting lithium from spodumene. U.S. Patent 3,112,170, 23 November 1963.
64. Archambault, M.; Olivier, C.A. Carbonatizing roast of lithium bearing ores. U.S. Patent 3,380,802, 30 April 1968.
65. Dunn, W.E.; Van Jahnke, J. Cyclical Vacuum Chlorination Processes, Including Lithium Extraction. U.S. Patent 7,588,741, 15 September 2009.
66. Medina, L.F.; El-Naggar, M.M.A.A. An alternative method for the recovery of lithium from spodumene. *Metall. Trans. B* **1984**, *15*, 725–726. [CrossRef]

67. Mast, E. Lithium Production from Spodumene. Master's Thesis, McGill University, Montréal, QC, USA, 1989.
68. Rezza, I.; Salinas, E.; Calvente, V.; Benuzzi, D.; De Tosetti, M.I.S. Extraction of lithium from spodumene by bioleaching. *Lett. Appl. Microbiol.* **1997**, *25*, 172–176. [CrossRef]
69. Chen, Y.; Tian, Q.; Chen, B.; Shi, X.; Liao, T. Preparation of lithium carbonate from spodumene by a sodium carbonate autoclave process. *Hydrometallurgy* **2011**, *109*, 43–46. [CrossRef]
70. Bieseki, L.; Melo, V.R.M.; Sobrinho, E.V.; Melo, D.M.A.; Pergher, S.B.C. Extração de lítio de amostras de β-espodumênio. *Cerâmica* **2013**, *59*, 557–562. [CrossRef]
71. Rosales, G.D.; Ruiz, M.D.C.; Rodriguez, M.H. Novel process for the extraction of lithium from -spodumene by leaching with HF. *Hydrometallurgy* **2014**, *147–148*, 1–6. [CrossRef]
72. Barbosa, L.I.; Valente, G.; Oorosco, R.P.; González, J.A. Lithium extraction from β-spodumene through chlorination with chlorine gas. *Miner. Eng.* **2014**, *56*, 29–34. [CrossRef]
73. Barbosa, L.I.; González, J.A.; Del Carmen Ruiz, M. Extraction of lithium from β-spodumene using chlorination roasting with calcium chloride. *Thermochim. Acta* **2015**, *605*, 63–67. [CrossRef]
74. Kuang, G.; Liu, Y.; Li, H.; Xing, S.; Li, F.; Guo, H. Extraction of lithium from β-spodumene unsing sodium sulphate solution. *Hydrometallurgy* **2018**, *177*, 49–56. [CrossRef]
75. Smith, J.C.; Harriott, P. *Unit Operations of Chemical Engineering*, 6th ed.; McGraw-Hill: New York, NY, USA, 1956; p. 966.
76. Gupta, C.K. *Chemical Metallurgy*; Principles and Practice, Wiley-VCH: Weinheim, Germany, 2003; p. 133.
77. Lajoie-Leroux, F.; Dessemond, C.; Soucy, G.; Laroche, N.; Magnan, J.F. Impact of the impurities on lithium extraction from β-spodumene in the sulphuric acid process. *Miner. Eng.* **2018**, *129*, 1–8. [CrossRef]
78. Botto, I.L.; Arazi, S.C.; Krenkel, T.G. Estudio cinético de la transformación polimórfica espodumeno I en espodumeno II. *Boletin dela Sociedad Española de Cerámica y Vidrio* **1975**, *14*, 225–230.
79. Mellor, J.W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume VI, Part II, Si, Silicates*, 1st ed.; Longmans, Green and Co. LTD: London, UK, 1930; 991p.
80. White, G.D.; McVoy, T.N. *Some Aspects of the Recovery of Lithium from Spodumene*; Oak Ridge National Laboratory: Oak Ridge, TN, USA, 1958; pp. 1–17.
81. Kotsupalo, N.P.; Menzheres, L.T.; Ryabtsev, A.D.; Boldyrev, V.V. Mechanical Activation of α-Spodumene for Further Processing into Lithium Compounds. *Theor. Found. Chem. Eng.* **2010**, *44*, 503–507. [CrossRef]
82. Salakjani, N.K.; Nikoloski, A.N.; Singh, P. Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 2: Microwave heating. *Miner. Eng.* **2017**, *100*, 191–199. [CrossRef]
83. Hatch, R.A. Phase Equilibrium in the system: Li_2O-Al_2O_3-SiO_2. *American Mineralogist* **1943**, *28*, 471–496.
84. Shoucri, A. *Étude de la Conversion α vers β d'un Minerai de Spodumene, Maîtrise*; Université de Sherbrooke: Sherbrooke, QC, Canada, 2015.
85. Dessemond, C.; Lajoie-Leroux, F.; Soucy, G.; Laroche, N.; Magnan, J.F. Revisiting the Traditionnal Process of Spodumene Conversion and Impact on Lithium Extraction. In *Proceedings of the First Global Conference on Extractive Metallurgy*; The Minerals, Metals and Materials Society: Pittsburgh, PA, USA, 2018; pp. 2281–2291.