

OPEN ACCESS

EDITED BY
Jon Telling,
Newcastle University, United Kingdom

REVIEWED BY
Nikolaos Koukouzas,
Centre for Research and Technology Hellas
(CERTH), Greece
Mário Gonçalves,
University of Lisbon, Portugal

*CORRESPONDENCE

RECEIVED 30 January 2024 ACCEPTED 05 April 2024 PUBLISHED 30 April 2024

CITATION

Hudson-Edwards KA (2024), Geochemistry and mineralogy of wastes from lithium-bearing granite-pegmatite mining: resource potential and environmental risks.

Front. Geochem. 2:1378996.
doi: 10.3389/faeoc.2024.1378996

© 2024 Hudson-Edwards. This is an open-

COPYRIGHT

access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.

Geochemistry and mineralogy of wastes from lithium-bearing granite-pegmatite mining: resource potential and environmental risks

Karen A. Hudson-Edwards*

Camborne School of Mines and Environment and Sustainability Institute, University of Exeter, Penryn, United Kingdom

The global need for lithium (Li) is increasing due to its use in batteries which are used to make electric vehicles, wind turbines and fuel cells to facilitate the world's 'green transition' to low carbon economies. The mining of Li, like that of other Earth materials, produces large volumes of waste such as tailings and processing chemicals. A growing body of research is addressing the resource potential and environmental impacts of wastes from mining of Li-bearing granites and pegmatites that produce around 40% of the world's Li. The wastes are dominated by SiO_2 and Al_2O_3 , with lesser Na_2O , K_2O and Fe_2O_3 , that are hosted in quartz, feldspar and micas. They can contain around 1 wt% Li₂O that is found in residual spodumene, lepidolite and zinnwaldite, and trace (<1 wt%) amounts of Rb, Cs, U and Be. Some exploitation of the Li from granite-pegmatite tailings is occurring on a commercial scale. There is also good potential for the waste quartz, feldspar and mica to be used in ceramics and building materials, and for the Rb, Cs and Be to be used for photovoltaic cells, alloys and other applications. Spodumene-bearing wastes can contain potentially toxic and/or radioactive U, Th and Tl, but the concentrations are generally low. Overall, Libearing granite-pegmatite mine wastes have good potential to be reused, remined and recycled. More research is required to characterize their geochemistry and mineralogy in detail to improve recovery and to understand how processing and weathering may affect environmental risk.

KEYWORDS

lithium, mine waste, granite, pegmatite, spodumene, lepidolite, quartz feldspar sand

1 Introduction

The mining industry produces huge volumes of waste because the economic commodities form only a small proportion of the materials extracted (Hudson-Edwards, 2016). A variety of solid wastes are produced, including coal and mineral fuels, sediment, overburden soil, mill tailings, processing chemicals and metallurgical slag (Hudson-Edwards et al., 2011). In 2022 the global amount of mine wastes was estimated to be around 268 billion tonnes, and this has been projected to increase to around 379 billion tonnes by 2030 (Research and Markets, 2024). The main reason for this is that most high-grade deposits have already mined, leading industry to exploit larger deposits with lower grades (Hudson-Edwards et al., 2011). A secondary reason is that there is increasing demand for Critical Raw Materials (CRMs), Earth materials with high

TABLE 1 Lithium-bearing minerals in Li-bearing granite-pegmatite ores and mine wastes. Adapted from Brown (2016) and Aylmore et al. (2018).

Mineral	Chemical formula	Li ₂ O (wt%)
Amblygonite	Li(F,OH)AlPO ₄	7.3-10.1
Eucryptite	LiAlSi ₄ O ₁₀	2.1-5.53
Hectorite	Na _{0.3} (Mg,Li) ₃ Si ₄ O ₁₀ (OH) ₂	0.54
Jadarite	LiNaSiB ₃ O ₇ (OH)	7.3
Lepidolite	(Li,Al) ₃ (Al,Si) ₄ O ₁₀ (F,OH) ₂	3.3-7.7
Petalite	LiAlSi ₄ O ₁₀	3.5-4.5
Polylithionite	KAl(Fe,Li)(Si ₃ Al)O ₁₀ (OH)F	2.0-7.7
Spodumene	LiAlSi ₂ O ₆	6.0-7.5
Zinnwaldite	(Li,Al,Fe) ₃ (Al,Si) ₄ O ₁₀ F ₂	2–5

economic and/or strategic importance for which there is no adequate substitute and a high supply risk (EC European Commission, 2014). CRMs are essential components for modern technologies such as batteries, photovoltaics, wind turbines, electronics, fuel cells, mobile phones, computers and other products, many of which are required to provide renewable energy as the world aims to reduce its reliance on fossil fuels.

Lithium (Li) is regarded by many countries as a CRM because it is a major component of Li-ion batteries that power electric vehicles and other electrical devices, and because it is currently mined in only a few countries. The World Bank Group predicted that the production of lithium could increase by 500% by 2050 to meet demand (World Bank Group, 2020). Around 60% of lithium is produced from salar brines, and the rest is extracted from 'hard rock' Li-bearing granites and pegmatites (Tadesse et al., 2019). Little is known about the salar Li mine wastes except that they are salts rich in all cations in the brines except Li (Vera et al., 2023). By contrast, wastes from Li-bearing granite and pegmatite mining are better studied and some are being exploited for Li and other commodities.

Knowledge of the geochemistry and mineralogy of wastes is essential for evaluating their potential for reuse, remining and recycling, in designing and optimising schemes to extract their economic components and in understanding and managing their environmental impacts (Brough et al., 2013; Jamieson et al., 2015). In this review the generation of Li-bearing granite-pegmatite wastes are outlined, and their geochemistry, mineralogy, resource potential and environmental impacts are described, and themes for future research are presented.

2 Lithium-bearing granite-pegmatite systems: Origin, extraction, processing

Li-bearing granites and pegmatites occur in every continent of the world except, to our knowledge, in Antarctica. The largest deposits are found in Australia, China and Brazil (Shaw, 2016). The parent magmas form at the post-collisional stage of orogenesis (Bradley et al., 2017), and the Li-bearing granites crystallise from these. Coarse-grained Li-bearing pegmatites are thought to form by crystallisation of highly fractionated melts that are derived from the granitic magmas (London, 2018; Li et al.,

2023), or anatexis of sedimentary rocks (Shaw et al., 2016; Müller et al., 2017) or Li-rich clays and borates (Simmons and Webber, 2008).

These rocks contain a variety of Li-bearing minerals that are summarised in Table 1. Lepidolite and zinnwaldite are the most common minerals in Li-granites, whereas spodumene and petalite are the main minerals found in pegmatites (Gourcerol et al., 2019). The other minerals shown in Table 1 occur in lesser amounts, mainly in pegmatites.

Despite their global occurrence, in 2022 Li-bearing granites and pegmatites were mined only in Australia (accounting for most of the production), China, Zimbabwe, Portugal and Canada (USGS, 2023). Spodumene was also recovered from tailings produced by AMG's tantalum Mibra Mine in Brazil (AMGLithium, 2024). In 2022, considerable exploration and development of Li-bearing granites and pegmatites was taking place globally (Australia, Austria, Brazil, Canada, China, Congo (Kinshasa), Czechia, Ethiopia, Finland, Germany, Ghana, Kazakhstan, Mali, Namibia, Nigeria, Peru, Portugal, Russia, Serbia, Spain, Thailand, Zimbabwe; (USGS, 2023), and so many more mines may be operational in the future.

Spodumene is the main Li-bearing mineral that is processed by industry due to its abundance and high Li content (Table 1) (Tadesse et al., 2019). It is concentrated using heavy media separation, froth flotation and/or magnetic separation processes (Amarante et al., 1999) To extract Li, spodumene concentrates undergo calcination at temperatures between 850°C and 1,100°C (Salakjani et al., 2016; Karrech et al., 2021b; Pickles and Marzoughi, 2022). This process causes the original monoclinic a-spodumene to transform to tetragonal β-spodumene that has a 30% larger structure and lower bulk density than the α -spodumene (Paris et al., 2023). These new properties allow the β-spodumene to be easily leached, often in concentrated sulfuric acid (H2SO4), resulting in the production of soluble Li₂SO₄ which is used to make Li hydroxide and Li carbonate (Salakjani et al., 2019). Digestion of the β-spodumene with HF and Ca(OH)₂ is also used to extract the Li (Rosales et al., 2014). The wastes produced from these processes are known as delithiated $\beta\mbox{-spodumene}$ (DβS) tailings (Karrech et al., 2021b; Karrech et al., 2021a).

Zinnwaldite can also be concentrated by flotation (Samková, 2009) and because it contains relatively high amounts of Fe (Table 2), by magnetic separation (Botula et al., 2005; Tadesse et al., 2019). The resulting concentrate can be calcined with CaCO₃ and leached with water. A very high quality (>99% pure) Li₂CO₃ concentrate can then be produced (Jandová et al., 2010). Lepidolite can also be concentrated using flotation, but it can be difficult to separate from muscovite due to their similar compositions (Tadesse et al., 2019). As with spodumene, lepidolite concentrates can also be digested in hot H₂SO₄ to recover Li. The resultant solutions can also contain K, Al, Rb and Cs, making separation and purification of the Li challenging (Li et al., 2019). Research is ongoing to attempt to crystallise the contaminating cations as mixed alums to provide a higher purity Li solution (Vieceli et al., 2018).

3 Geochemistry of Li-bearing granitepegmatite wastes

The major and trace element geochemical compositions of a range of wastes from lithium (spodumene), Sn-W and kaolinite

TABLE 2 Geochemistry of a range of Li-bearing granite-pegmatite mine wastes. All values in wt.%.

Waste	Jiajika lithium mine tailings, China (Tian et al., 2018)	Transbaikal mining- and-processing integrated works, Russia (Yusupov et al., 2015)	Spodumene- pegmatite flotation tailings, Whabouchi mine project Québec, Canada (Roy et al., 2023)	Quartz feldspar sand (QFS) tailings from spodumene concentration, Keliber Oy, Finland (Lemougna et al., 2019b)	Delithiated β- spodumene (DβS-Covalent) tailings, Australia (Karrech et al., 2021b; Karrech et al., 2021a)	Spodumene tailings from spodumene processing plant, Jiangxi Province, China (Bian et al., 2023)	Zinnwaldite waste from dressing of Sn–W ores, Cinovec, Czech republic (Jandova et al., 2010)
Deposit type	Pegmatite	Pegmatite	Pegmatite	Pegmatite	Pegmatite	Pegmatite	Sn-W
Major Li mineral	Spodumene	Spodumene	Spodumene	Spodumene	Spodumene	Spodumene	Zinnwaldite
Li ₂ O	0.17	0.26	0.97			1.02	0.45
SiO ₂	76.4	77.8	>64.0	77.5	62.0	69.2	65.3
Al ₂ O ₃	14.2	12.9	14.9	13.5	20.8	21.5	25.1
Fe ₂ O ₃	0.86	0.41	0.88	0.2	1.4	0.61	8.39
MnO		0.02	0.11		0.2		
MgO		<0.10			0.5		
CaO		0.36	0.28	0.3		0.68	0.88
Na ₂ O	5.14	4.69	3.57	4.8	0.6	3.14	0.40
K ₂ O	2.23	2.55	2.53	3.3	0.6	2.92	13.2
TiO ₂		0.04		0.0	0.6	0.27	
P ₂ O ₅		0.10		0.1	0.3	0.78	
Cs ₂ O							0.11
Rb ₂ O						0.19	0.22
SO ₃		<0.03			3.9		
LOI		0.80					
Waste	53 µm-500 µm size fraction kaolinite mine waste, new sink G5, St Austell, Cornwall, United Kingdom (lqbal, 2015)	53 µm-500 µm size fraction kaolinite mine waste, stope 13 G4, St Austell, Cornwall, United Kingdom (Iqbal, 2015)	Lepidolite flotation reject, Alvarroes- Goncalo (Sousa et al., 2018)	>1,000 µm size fraction kaolinite mine waste, Beauvoir, France (Igbal, 2015)	>1,000 µm size fraction kaolinite mine waste, Beauvoir, France (lqbal, 2015)	>1,000 µm size fraction kaolinite mine waste, Beauvoir, France (qbal, 2015)	Nb-Ta tailings, Yichun tantalum and niobium mine tailing dam, Jiangxi Province, China (Huang et al., 2020)
Deposit type	Kaolinised granite	Kaolinised granite	Pegmatite	Kaolinised granite	Kaolinised granite	Kaolinised granite	Nb-Ta
Deposit type Major Li mineral	Kaolinised granite Zinnwaldite	Kaolinised granite Zinnwaldite	Pegmatite Lepidolite	Kaolinised granite Lepidolite	Kaolinised granite Lepidolite	Kaolinised granite Lepidolite	Nb-Ta Lepidolite
Major Li	_				-	-	
Major Li mineral	Zinnwaldite	Zinnwaldite	Lepidolite	Lepidolite	Lepidolite	Lepidolite	Lepidolite
Major Li mineral Li ₂ O	Zinnwaldite	Zinnwaldite	Lepidolite	Lepidolite	Lepidolite	Lepidolite	Lepidolite
Major Li mineral Li ₂ O SiO ₂	Zinnwaldite 0.09 81.0	Zinnwaldite 0.02 50.7	Lepidolite 0.61 74.6	Lepidolite 1.1 81.5	Lepidolite 1.3 70.3	Lepidolite 0.8 66.0	Lepidolite 0.61 70.1
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃	Zinnwaldite 0.09 81.0 8.29	Zinnwaldite 0.02 50.7 27.0	Lepidolite 0.61 74.6	Lepidolite 1.1 81.5	Lepidolite 1.3 70.3 18.3	Lepidolite 0.8 66.0	Lepidolite 0.61 70.1 19.8
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃	Zinnwaldite 0.09 81.0 8.29	Zinnwaldite 0.02 50.7 27.0	Lepidolite 0.61 74.6	Lepidolite 1.1 81.5	Lepidolite 1.3 70.3 18.3	Lepidolite 0.8 66.0	Lepidolite 0.61 70.1 19.8
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃	Zinnwaldite 0.09 81.0 8.29	Zinnwaldite 0.02 50.7 27.0	Lepidolite 0.61 74.6	Lepidolite 1.1 81.5	Lepidolite 1.3 70.3 18.3	Lepidolite 0.8 66.0	Lepidolite 0.61 70.1 19.8
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO	Zinnwaldite 0.09 81.0 8.29	Zinnwaldite 0.02 50.7 27.0	Lepidolite 0.61 74.6	Lepidolite 1.1 81.5 11.0 0.2	Lepidolite 1.3 70.3 18.3 0.2	Lepidolite 0.8 66.0 19.7 0.1	Lepidolite 0.61 70.1 19.8
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO	Zinnwaldite 0.09 81.0 8.29	Zinnwaldite 0.02 50.7 27.0	Lepidolite 0.61 74.6 14.8 0.19	Lepidolite 1.1 81.5 11.0 0.2	Lepidolite 1.3 70.3 18.3 0.2	Lepidolite 0.8 66.0 19.7 0.1	Lepidolite 0.61 70.1 19.8 0.76
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO CaO	Zinnwaldite 0.09 81.0 8.29	Zinnwaldite 0.02 50.7 27.0	Lepidolite 0.61 74.6 14.8 0.19	Lepidolite 1.1 81.5 11.0 0.2 0.1 1.2	Lepidolite 1.3 70.3 18.3 0.2 0.1 4.2	Lepidolite 0.8 66.0 19.7 0.1 0.1 6.7	Lepidolite 0.61 70.1 19.8 0.76
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO CaO Na ₂ O	Zinnwaldite 0.09 81.0 8.29 3.81	Zinnwaldite 0.02 50.7 27.0 6.5	Lepidolite 0.61 74.6 14.8 0.19	Lepidolite 1.1 81.5 11.0 0.2 0.1 1.2	Lepidolite 1.3 70.3 18.3 0.2 0.1 4.2	Lepidolite 0.8 66.0 19.7 0.1 0.1 6.7	Lepidolite 0.61 70.1 19.8 0.76
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO CaO Na ₂ O K ₂ O	Zinnwaldite 0.09 81.0 8.29 3.81	Zinnwaldite 0.02 50.7 27.0 6.5	Lepidolite 0.61 74.6 14.8 0.19	Lepidolite 1.1 81.5 11.0 0.2 0.1 1.2	Lepidolite 1.3 70.3 18.3 0.2 0.1 4.2	Lepidolite 0.8 66.0 19.7 0.1 0.1 6.7	Lepidolite 0.61 70.1 19.8 0.76
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO CaO Na ₂ O TiO ₂ P ₂ O ₅	Zinnwaldite 0.09 81.0 8.29 3.81	Zinnwaldite 0.02 50.7 27.0 6.5	Lepidolite 0.61 74.6 14.8 0.19	Lepidolite 1.1 81.5 11.0 0.2 0.1 1.2	Lepidolite 1.3 70.3 18.3 0.2 0.1 4.2	Lepidolite 0.8 66.0 19.7 0.1 0.1 6.7	Lepidolite 0.61 70.1 19.8 0.76
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO CaO Na ₂ O K ₂ O TiO ₂ P ₂ O ₅ Cs ₂ O	Zinnwaldite 0.09 81.0 8.29 3.81	Zinnwaldite 0.02 50.7 27.0 6.5	Lepidolite 0.61 74.6 14.8 0.19	Lepidolite 1.1 81.5 11.0 0.2 0.1 1.2	Lepidolite 1.3 70.3 18.3 0.2 0.1 4.2	Lepidolite 0.8 66.0 19.7 0.1 0.1 6.7	Lepidolite 0.61 70.1 19.8 0.76
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO CaO Na ₂ O K ₂ O TiO ₂ P ₂ O ₅ Cs ₂ O Rb ₂ O	Zinnwaldite 0.09 81.0 8.29 3.81	Zinnwaldite 0.02 50.7 27.0 6.5	Lepidolite 0.61 74.6 14.8 0.19	Lepidolite 1.1 81.5 11.0 0.2 0.1 1.2	Lepidolite 1.3 70.3 18.3 0.2 0.1 4.2	Lepidolite 0.8 66.0 19.7 0.1 0.1 6.7	Lepidolite 0.61 70.1 19.8 0.76 5.38 2.98
Major Li mineral Li ₂ O SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MnO MgO CaO Na ₂ O K ₂ O TiO ₂ P ₂ O ₃ Cs ₂ O Rb ₂ O Nb ₂ O ₅	Zinnwaldite 0.09 81.0 8.29 3.81	Zinnwaldite 0.02 50.7 27.0 6.5	Lepidolite 0.61 74.6 14.8 0.19 4.65 1.96	Lepidolite 1.1 81.5 11.0 0.2 0.1 1.2	Lepidolite 1.3 70.3 18.3 0.2 0.1 4.2	Lepidolite 0.8 66.0 19.7 0.1 0.1 6.7	Lepidolite 0.61 70.1 19.8 0.76 5.38 2.98



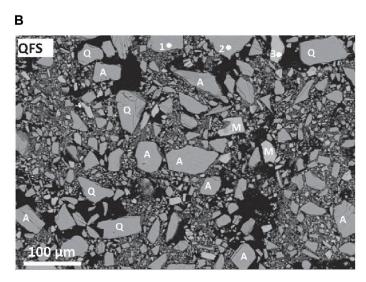


FIGURE 1
(A) Lithium-bearing wastes in former kaolinite mine pit, Cornwall, United Kingdom (B) scanning electron microscope (SEM) photomicrograph of quartz feldspar sand (QFS) from spodumene tailings waste. Q: quartz, (A) albite, M: microcline. Numbered stars show point that were analysed to determine mineral composition. Reprinted from *Minerals Engineering*, 141, Lemougna, P.N. et al., Spodumene tailings for porcelain and structural materials: Effect of temperature (1,050°C-1,200°C) on the sintering and properties, 105,843, Copyright (2019), with permission from Elsevier.

mining are summarised in Table 2. All wastes have high concentrations of SiO_2 (50.7–81.5 wt%) and Al_2O_3 (8.29–27.0 wt%) and moderate concentrations of Na_2O (0.4–6.7 wt%), K_2O (0.6–13.2 wt%) and Fe_2O_3 (0.1–8.39 wt%). Variable but low (<1 wt%) concentrations of CaO, MgO, TiO_2 , P_2O_5 , BeO, Rb_2O and SO_3 have also been reported. Lithium oxide (Li₂O) concentrations range from 0.02 to 1.3 wt%. Concentrations of potentially toxic metal (loids) such as As, Cd, Cu, Pb and Zn are generally not reported for Li-bearing granite-pegmatite wastes, but when they are, they tend to be very low (Lemougna et al., 2019a). Concentrations of U, Th and Tl are discussed in the Environmental Impacts section of this paper.

Lithium-bearing granite-pegmatite wastes are normally white in colour (Figure 1A) and fine-grained, with heterogeneous grain sizes and angular shapes (Figure 1B). The major (>5 vol%) and minor (<5 vol%) minerals in the wastes are summarised in Table 3. Quartz, plagioclase, K-feldspar and muscovite are the major minerals present and account for the high to moderate concentrations of SiO_2 , Al_2O_3 , Na_2O and K_2O in the wastes (Table 2). Minerals such as Nb-Ta oxides (Table 3) account for the minor amounts of Nb_2O_5 and Ta_2O_5 present (Table 2).

Most of the mineralogical determination of Li-bearing granite-pegmatite wastes is done using X-ray diffraction (e.g., (Lemougna et al., 2019b; Karrech et al., 2021a). While this method can identify minerals, it does not give information on their trace element compositions. Roy

et al. (2023) sampled spodumene from the raw ore, concentrator feed and tailings from density separation and spodumene flotation at the Whabouchi mine project in Québec, Canada. They conducted extensive mineralogical analysis using automated mineralogical analysis with a QEMSCAN[™] instrument, scanning electron microscopy (SEM) with energy dispersive spectrometers (EDS) and electron probe micro analysis (EPMA) for major and trace element chemical analysis, respectively. They showed that the processing reduced the amount of spodumene from ore to tailings but did not alter mineral compositions. Many of the minerals were shown to have trace impurities. The spodumene, for example, contained trace amounts of Fe, Mn and Nb whereas the petalite did not. Nb-Ta oxides ranged in composition from columbite-rich ((Fe,Mn)(Nb>>Ta)O₆) to pure tantalite ((Fe,Mn)TaO₆), and contained trace Ti, Sn and U. Such data are useful in evaluating the resource potential and environmental impact of the wastes.

4 Resource potential

4.1 Lithium

The Li concentrations in the granite-pegmatite wastes (Table 2) have been considered high enough for researchers and industry to find optimal methods for their reprocessing. Froth flotation has been

TABLE 3 Resource potential and environmental risk of minerals in Li-bearing granite-pegmatite mine wastes.

Mineral	Chemical formula	Waste type occurrence	Resource potential	Environmental risk
Major mineral	ls (>5 vol%)			
Quartz	SiO ₂	spodumene	DβS for construction and geotechnical materials; QFS	
		Sn-W kaolinite	for ceramics geopolymers, cement mortar, aggregate	
		Nb-Ta		
Plagioclase	(Na _{1-x} Ca _x)Si ₃ AlO ₈	spodumene	DβS for construction and geotechnical materials; QFS	
		Sn-W kaolinite	for ceramics geopolymers, cement mortar, aggregate	
		Nb-Ta		
K-feldspar	KAlSi ₃ O ₈	spodumene	$D\beta S$ for construction and geotechnical materials; QFS	
		Sn-W kaolinite	for ceramics geopolymers, cement mortar, aggregate	
		Nb-Ta		
Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	spodumene	$D\beta S$ for construction and geotechnical materials; QFS	
		Sn-W kaolinite	for ceramics geopolymers, cement mortar aggregate	
		Nb-Ta		
Minor mineral	ls (<5 vol%)			
Ankerite	Ca(Fe,Mg,Mn)(CO ₃) ₂	spodumene		
Beryl	Be ₃ Al ₂ Si ₆ O ₁₈	spodumene	alloys	
Fluorite	CaF ₂	spodumene		
Garnet	(Ca,Mg,Fe,Mn) ₃ (Fe,Al,Cr) ₆ (SiO ₄) ₃	spodumene		
Lepidolite	(Li,Al) ₃ (Al,Si) ₄ O ₁₀ (F,OH) ₂	kaolinite	Li for batteries, ceramics, glass, greases, polymers	
		Nb-Ta	Rb for photovoltaic cells	
Nb-Ta oxides	various	spodumene		
Spodumene	LiAlSi ₂ O ₆	spodumene	Li for batteries, ceramics, glass, greases, polymers	
			Rb for photovoltaic cells	
Uraninite	UO ₂	spodumene		Radioactivity and toxicity
U-bearing zircon	U-bearing ZrSiO ₄	spodumene		Radioactivity and toxicity
Zinnwaldite	(Li,Al,Fe) ₃ (Al,Si) ₄ O ₁₀ F ₂	Sn-W	Li for batteries, ceramics, glass, greases, polymers	
		kaolinite	Rb for photovoltaic cells	

successfully shown to concentrate the spodumene (Yusupov et al., 2015; Tian et al., 2018), lepidolite (He et al., 2013; Sousa et al., 2018) and zinnwaldite (Samková, 2009; Jandová et al., 2010; Siame and Pascoe, 2011) from these wastes to upgrade their Li content (Table 3). Flotation can be followed by magnetic separation to further increase the amount of Li in the concentrate to around 4.5–6.0 wt% Li₂O (Siame and Pascoe, 2011; Yusupov et al., 2015; Tian et al., 2018). The remaining feldspars and quartz can also be separated by flotation and used for other products (Sousa et al., 2018; Tian et al., 2018)(see next section). These combined actions can use of the majority of the wastes produced from the primary mining (e.g., 70%; Tian et al. (2018)).

The resultant Li waste concentrate can be processed using similar methods to those used for primary Li ores. This can involve roasting with additives such as limestone, gypsum and sodium sulfate (Siame and Pascoe, 2011). This process is followed by leaching with H_2SO_4 or other acids (e.g., HF) at moderate to high temperatures to recover the Li and make it into saleable products such as Li_2CO_3 and Li(OH) (Jandová et al., 2010).

4.2 Quartz, feldspar and mica

The resource potential of the quartz, feldspar and mica components of Li-bearing granite-pegmatite wastes have been evaluated by several researchers. Two types of wastes have been studied: D β S tailings (Karrech et al., 2021b; Karrech et al., 2021a) and quartz and feldspar rich tailings from spodumene tailings, known as quartz feldspar sand (QFS) (Lemougna et al., 2019a; Lemougna

et al., 2019b; Lemougna et al., 2020). D β S has been characterised as a silt loam with variably shaped and sharp-edged grains (Karrech et al., 2021a). It requires addition of granulated blast furnace slag to make construction and geotechnical materials. When such mixtures are made, often with other wastes such as fly ash, the addition of D β S has been shown to increase workability and setting time, and to reduce shrinkage (Karrech et al., 2021b; Karrech et al., 2021a).

QFS has been evaluated as a raw material for ceramic production. Lemougna et al. (2019a), Lemougna et al. (2019b) and Lemougna et al. (2020) carried out experiments using QFS from Keliber Oy in Finland to evaluate its suitability for porcelain and construction materials. The QFS comprised quartz, albite, microcline and minor muscovite (Table 3). QFS was combined with kaolinite (Lemougna et al., 2019b), ladle slag (Lemougna et al., 2019a) and glass wool waste (Lemougna et al., 2020) and analysed to determine optimal mixtures for porcelain, brick and construction materials, respectively. Grinding of some of the components, sintering temperatures, secondary mineral formation and addition of fluxes such as sodium hydroxide and carbonate were the major factors affecting the density and strength of the final products. It was concluded that QFS had significant potential to be used as a resource.

4.3 Rubidium, caesium and beryllium

Lithium lies in Group 1 of the Periodic Table can be substituted in minerals by other elements in this group. One of these is Rb, which is known to occur in spodumene, lepidolite and zinnwaldite (Kunasz, 2006). Rb₂O concentrations between 0.17 and 0.40 wt% have been reported in lepidolite- and zinnwaldite-bearing wastes from Sn-W and kaolinite mining (Table 1). The Rb can be recovered from these minerals when processing for Li (Buttermann and Reese Jr, 2003). Jandová et al. (2010), for example, recovered Rb by roasting zinnwaldite concentrates containing 1.21wt% Li and 0.84wt% Rb with CaCO₃ and leaching the produced calcine with water. The concentrate was prepared from zinnwaldite wastes containing 0.21wt% Li and 0.20wt% Rb that were generated through the processing of Sn-W ores. Notable concentrations of Rb₂O have been documented in spodumene tailings (Melentiev et al., 2022; Roy et al., 2023) (Table 2), and Rb is also known to occur in muscovite, which is present in all Li-bearing granitepegmatite mine wastes documented in Table 2. As a result, many authors have suggested that these wastes may be suitable exploration targets for Rb that could be used in photovoltaic cells and other applications (Siame and Pascoe, 2011; Iqbal, 2015; Melentiev et al., 2022; Bian et al., 2023).

Trace concentrations of Cs (0.11 wt%) have been found in zinnwaldite-bearing wastes from the dressing of Sn-W ores (Jandová et al., 2010). Samková (2009) demonstrated that the zinnwaldite from such wastes could be effectively separated using flotation with an amine-based cationic collector at laboratory scale.

The mineral beryl has been found in spodumene tailings (Table 3) and has been proposed to be a source of Be for alloys (Browning et al., 1964; Melentiev et al., 2022). Browning et al. (1964) showed that it could be recovered using an HF activator and an oleic acid collector.

5 Potential environmental impacts

The potential environmental impacts of the minerals and their included elements are summarised in Table 3. Kinetic leach testing of spodumene-bearing tailings from the Whabouchi mine project in Québec, Canada, produced waters with mg to sub-mg/L amounts of U (Roy et al., 2023). These were attributed to the weathering of primary uraninite and U-rich zircon in the tailings in the presence of a Cabearing fluid. Phases with uranophane (Ca(UO₂)₂SiO₃(OH)₂·5H₂O) compositions and U-Ca-phosphates were found in filling voids and fractures in spodumene tailings, and were proposed to precipitate from these fluids. Overall, however, the U concentrations in these wastes (2.97–5.28 mg/kg) are well below Canadian Soil Guideline Values of 23–300 mg/kg (CCME, 2024).

Other potentially ecotoxic elements have been found Li-bearing granite-pegmatite tailings. Melentiev et al. (2022) detected Tl (1.51–5.49 mg/kg) in spodumene tailings from the Zabaikalsk mining and processing plant in Russia. Thallium (1.2–2.8 mg/kg) was also found in the Whabouchi tailings, in addition to minor amounts of Th (1.2–2.8 mg/kg) (Roy et al., 2022).

Sulfur contents of Li-bearing granite/pegmatite wastes are not always reported, but those available are low (Table 2), suggesting that the wastes will not generate acid. This is confirmed by paste pH and leaching tests that yield waters with pH values between eight and nine (e.g., Chen and Goulet, 2022; Roy et al., 2022).

The evolution of spodumene flotation and analcimecontaining tailings from the former Quebec Lithium Corporation site in La Corne, Quebec, Canada during 55 years of storage was evaluated by (Roy et al., 2022). Textural analysis and sequential extraction data suggested that the tailings had not been significantly weathered nor formed secondary minerals. Despite this, elevated concentrations of Li, Al, K, Rb and Be were found in the chemical extractant solutions derived from the analcime tailings. These were suggested to result from the acid roasting and pressured alkaline leaching that the materials had experienced, which would have made them more susceptible to breakdown. High (mg/L-level) concentrations of Li in the tailings porewaters may have been due to this process, but their environmental impacts were unknown. Chen and Goulet (2022) compared metal concentrations from static and kinetic leach tests on wastes from three unnamed proposed spodumene Li mines in Quebec to Canadian and USA groundwater and aquatic life water quality guidelines. They found that some of the As, Cu and Li concentrations were above the guideline values. Based on their analysis, they recommended that the As and Cu data should be used in environmental risk assessment models and that Li toxicity testing should be conducted to optimise mine waste management.

The published studies of Roy et al. (2022), Roy et al. (2023) and Chen and Goulet (2022) are, to the author's knowledge, the few that have evaluated the long-term stability and potential impacts of Li granite-pegmatite mine wastes and related these to potential environmental impacts. Given the potential increase in hard-rock Li mining that may occur in the 2020s and 2030s, more research is needed, especially as high concentrations of Li have been found in other mining-affected areas (e.g., 13 mg/L Li in mine drainage; Aral and Veccio-Sadus (2008)).

6 Summary and outlook

Mine wastes generated from Li-bearing granite and pegmatite extraction and processing have high contents of SiO₂ and Al₂O₃, and moderate contents of Na₂O, K₂O and Fe₂O₃, which are hosted in quartz, feldspar and micas. They also contain 0.02 to 1.3 wt% Li₂O that is found in residual spodumene, lepidolite and zinnwaldite. A growing body of research has shown that there is significant potential for the wastes to be reused, remined and recycled to recover Li, quartz-feldspar sand, Rb, Cs and Be for a variety of applications. Overall the wastes are not toxic nor acid-generating, but some contain U and Th that may generate radioactivity.

Although bulk geochemical and mineralogical data for the Libearing granite/pegmatite wastes are documented in the literature, they are insufficient for understanding the effects of processing and weathering on the potential mobility of elements from the wastes, and for understanding how the presence of mineral impurities may affect the quality and stability of reuse, recycling or remining products (Table 3). Detailed mineral chemical and textural evidence such as that presented in Roy et al. (2022) and Roy et al. (2023) is required for these wastes to enable their full resource and environmental risk potentials to be evaluated. This information can be combined with geochemical data and leaching tests to understand the geochemical behaviour of the wastes and their products (Parbhakar-Fox et al., 2013; Jamieson et al., 2015), and in turn potentially increase the market value and demand for the latter

Author contributions

KH-E: Writing-original draft, Writing-review and editing.

References

Amarante, M. M., De Sousa, A. B., and Leite, M. M. (1999). Processing a spodumene ore to obtain lithium concentrates for addition to glass and ceramic bodies. *Miner. Eng.* 12, 433–436. doi:10.1016/s0892-6875(99)00023-0

AMGLITHIUM (2024). AMGLIthium. Available at: https://amglithium.com/(Accessed January 28, 2024).

Aral, H., and Vecchio-Sadus, A. (2008). Toxicity of lithium to humans and the environment-A literature review. *Ecotoxicol. Environ. Saf.* 70, 349–356. doi:10.1016/j. ecoenv.2008.02.026

Aylmore, M. G., Merigot, K., Quadir, Z., Rickard, W. D. A., Evans, N. J., Mcdonald, B. J., et al. (2018). Applications of advanced analytical and mass spectrometry techniques to the characterisation of micaceous lithium-bearing ores. *Miner. Eng.* 116, 182–195. doi:10.1016/j.mineng.2017.08.004

Bian, Z., Zhang, H., Ye, J., and Ning, Z. (2023). Flotation behavior of oleate and dodecylamine as mixed collector for recovery of lithium and rubidium from low-grade spodumene tailings: experiment, characterization and DFT calculation. *Appl. Surf. Sci.* 638, 158117. doi:10.1016/j.apsusc.2023.158117

Botula, J., Rucký, P., and Řepka, V. (2005). Extraction of zinnwaldite from mining and processing wastes.

Bradley, D. C., Mccauley, A. D., and Stillings, L. L. (2017). "Mineral-deposit model for lithium-cesium-tantalum pegmatites." in *Mineral deposit models for resource assessment* (11885).

Brough, C. P., Warrender, R., Bowell, R. J., Barnes, A., and Parbhakar-Fox, A. (2013). The process mineralogy of mine wastes. *Miner. Eng.* 52, 125–135. doi:10.1016/j.mineng. 2013.05.003

Browning, J. S., Bennett, P. E., and Mcvay, T. L. (1964). Continuous flotation of beryl from spodumene mill tailings. Kings Mountain, N.C. Washington: Foote Mineral Company.

Brown, T. (2016). Lithium.

Buttermann, W. C., and Reese, R. G. (2003). Mineral commodity profiles rubidium. Open File Report 03-045. U.S. Geological Survey.

Funding

The author(s) declare financial support was received for the research, authorship, and/or publication of this article. This review is supported by the UK's Natural Environment Research Council funded Lithium for Future Technology (LiFT) project (NE/V007009/1).

Acknowledgments

KHE thanks members of the LiFT research team for support.

Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The author(s) declared that they were an editorial board member of Frontiers, at the time of submission. This had no impact on the peer review process and the final decision.

Publisher's note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Ccme, C. C. O. M. O. T. E. (2024). Canadian environmental quality guidelines (CEQGs). Available at: https://ccme.ca/en/current-activities/canadian-environmental-quality-guidelines (Accessed January 9, 2024).

Chen, R., and Goulet, R. R. (2022). "Identifying potential contaminants of concern in lithium mine waste to limit environmental impacts," in 12th ICARD International Conference on Acid Rock Drainage, Virtual Australia, September 21, 2022.

EC (EUROPEAN COMMISSION (2014). EU commission, 2014. Report on critical raw materials for the EU. Report of the ad-hoc working Group on defining critical raw materials.

Gourcerol, B., Gloaguen, E., Melleton, J., Tuduri, J., and Galiegue, X. (2019). Reassessing the European lithium resource potential - a review of hard-rock resources and metallogeny. *Ore Geol. Rev.* 109, 494–519. doi:10.1016/j.oregeorev.2019. 04.015

He, G. C., Feng, J. N., Mao, M. X., and Wu, Y. P. (2013). Application of combined collectors in flotation of lepidolite. *Adv. Mater. Res.* 734-737, 921–924. doi:10.4028/www.scientific.net/amr.734-737.921

Huang, Z., Zhang, S., Cheng, C., Wang, H., Liu, R., Hu, Y., et al. (2020). Recycling lepidolite from tantalum–niobium mine tailings by a combined magnetic–flotation process using a novel Gemini surfactant: from tailings dams to the "bling" raw material of lithium. ACS Sustain. Chem. Eng. 8, 18206–18214. doi:10.1021/acssuschemeng.0c06609

Hudson-Edwards, K. A. (2016). Tackling mine wastes. Science 352, 288–290. doi:10. 1126/science.aaf3354

Hudson-Edwards, K. A., Jamieson, H. E., and Lottermoser, B. G. (2011). Mine wastes: past, present, future. *Elements* 7, 375–380. doi:10.2113/gselements.7.6.375

Iqbal, Z. (2015). Recovery of lithium from kaolin mining waste material (Birmingham, UK: University of Birmingham). PhD.

Jamieson, H. E., Walker, S. R., and Parsons, M. B. (2015). Mineralogical characterization of mine waste. *Appl. Geochem.* 57, 85–105. doi:10.1016/j. apgeochem.2014.12.014

Jandová, J., Dvořák, P., and Vu, H. N. (2010). Processing of zinnwaldite waste to obtain Li_2CO_3 . $\textit{Hydrometallurgy}\ 103,\ 12–18.\ doi:10.1016/j.hydromet.2010.02.010$

Karrech, A., Dong, M., Skut, J., Elchalakani, M., and Shahin, M. A. (2021a). Management and valorisation of delithiated β -spodumene and its processing stream. *Case Stud. Constr. Mater.* 15, e00671. doi:10.1016/j.cscm.2021.e00671

Karrech, A., Dong, M., Skut, J., Elchalakani, M., and Shahin, M. (2021b). Delithiated β -spodumene as a geopolymer precursor. *Constr. Build. Mater.* 309, 124974. doi:10. 1016/j.conbuildmat.2021.124974

Kunasz, I. (2006). "Lithium resources," in *Industrial minerals and rocks* Editors J. E. KOGEL, N. C. TRIVEDI, J. M. BARKER, and S. T. KRUKOWSKI 7 (Littleton, Colorado, USA: Society for Mining, Metallurgy and Exploration Inc).

Lemougna, P. N., Yliniemi, J., Ismailov, A., Levanen, E., Tanskanen, P., Kinnunen, P., et al. (2019a). Recycling lithium mine tailings in the production of low temperature (700–900 °C) ceramics: Effect of ladle slag and sodium compounds on the processing and final properties. *Constr. Build. Mater.* 221, 332–344. doi:10.1016/j.conbuildmat. 2019.06.078

Lemougna, P. N., Yliniemi, J., Ismailov, A., Levanen, E., Tanskanen, P., Kinnunen, P., et al. (2019b). Spodumene tailings for porcelain and structural materials: Effect of temperature (1050–1200 °C) on the sintering and properties. *Miner. Eng.* 141, 105843. doi:10.1016/j.mineng.2019.105843

Lemougna, P. N., Yliniemi, J., Nguyen, H., Adesanya, E., Tanskanen, P., Kinnunen, P., et al. (2020). Utilisation of glass wool waste and mine tailings in high performance building ceramics. *J. Build. Eng.* 31, 101383. doi:10.1016/j.jobe.2020.101383

Li, B., Zhao, L., Lu, A.-H., Luo, J.-B., Kong, H., and Lai, J.-Q. (2024). Mineralogical constraints on pegmatite genesis and rare metal mineralization in the Mufushan batholith, South China. *Ore Geol. Rev.* 164, 105856. doi:10.1016/j.oregeorev.2023.105856

Li, H., Eksteen, J., and Kuang, G. (2019). Recovery of lithium from mineral resources: state-of-the-art and perspectives – a review. *Hydrometallurgy* 189, 105129. doi:10.1016/j.hydromet.2019.105129

London, D. (2018). Ore-forming processes within granitic pegmatites. *Ore Geol. Rev.* 101, 349–383. doi:10.1016/j.oregeorev.2018.04.020

Melentiev, G. B., Yurgenson, G. A., and Delitzyn, L. M. (2022). Prospects and priorities for the reconstruction and development of lithium mining production on the basis of domestic raw materials. Лволюция биосферы и течноГенез. Материалы Всероссийской конференции с международным участием 962, 012055. doi:10.57245/978_5_9293_3064_3_2022_1_218

Müller, A., Romer, R. L., and Pedersen, R.-B. (2017). The Sveconorwegian pegmatite province – thousands of pegmatites without parental granites. *Can. Mineralogist* 55, 283–315. doi:10.3749/canmin.1600075

Parbhakar-Fox, A., Lottermoser, B., and Bradshaw, D. (2013). Evaluating waste rock mineralogy and microtexture during kinetic testing for improved acid rock drainage prediction. *Miner. Eng.* 52, 111–124. doi:10.1016/j.mineng. 2013.04.022

Paris, J., Mohammadi-Jam, S., Li, R., Liang, J., Oh, H. J., Kökkiliç, O., et al. (2023). "Preliminary investigation into lithium extraction by phosphoric acid leaching of spodumene," in *Sustainable minerals* (United Kingdom: Falmouth).

Pickles, C. A., and Marzoughi, O. (2022). Thermodynamic modelling of spodumene decrepitation. *Mineral Process. Extr. Metallurgy* 131, 130–144. doi:10.1080/25726641. 2020.1827675

RESEARCH AND MARKETS (2024). Mining waste management - global strategic business report.

Rosales, G. D., Ruiz, M. D. C., and Rodriguez, M. H. (2014). Novel process for the extraction of lithium from β -spodumene by leaching with HF. *Hydrometallurgy* 147-148, 1–6. doi:10.1016/j.hydromet.2014.04.009

Roy, T., Plante, B., Benzaazoua, M., and Demers, I. (2023). Geochemistry and mineralogy of a spodumene-pegmatite lithium ore at various mineral beneficiation stages. *Miner. Eng.* 202, 108312. doi:10.1016/j.mineng.2023.108312

Roy, T., Plante, B., Benzaazoua, M., Demers, I., Coudert, L., and Turcotte, S. (2022). Geochemistry of decades-old spodumene mine tailings under a humid continental climate. *Appl. Geochem.* 146, 105481. doi:10.1016/j.apgeochem.2022.105481

Salakjani, N. K., Singh, P., and Nikoloski, A. N. (2016). Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: conventional heating. *Miner. Eng.* 98, 71–79. doi:10.1016/j.mineng.2016.07.018

Salakjani, N. K., Singh, P., and Nikoloski, A. N. (2019). Production of lithium - a literature review. Part 2. Extraction from spodumene. *Mineral Process. Extr. Metallurgy Rev.* 42, 268–283. doi:10.1080/08827508.2019.1700984

Samková, R. (2009). Recovering lithium mica from the waste after mining Sn-W ores through the use of flotation. *Geosci. Eng. LV*, 33-37.

Shaw, R. A., Goodenough, K. M., Roberts, N. M. W., Horstwood, M. S. A., Chenery, S. R., and Gunn, A. G. (2016). Petrogenesis of rare-metal pegmatites in high-grade metamorphic terranes: a case study from the Lewisian Gneiss Complex of north-west Scotland. *Precambrian Res.* 281, 338–362. doi:10.1016/j.precamres. 2016.06.008

Siame, E., and Pascoe, R. D. (2011). Extraction of lithium from micaceous waste from China clay production. *Miner. Eng.* 24, 1595–1602. doi:10.1016/j.mineng.2011.08.013

Simmons, W. B. S., and Webber, K. L. (2008). Pegmatite genesis: state of the art. *Eur. J. Mineralogy* 20, 421–438. doi:10.1127/0935-1221/2008/0020-1833

Sousa, R., Ramos, V., Guedes, A., Noronha, F., Botelho de Sousa, A., Machado Leite, M., et al. (2018). The Alvarrões-Gonçalo Li project: an example of sustainable lithium mining. *Adv. Geosciences* 45, 1–5. doi:10.5194/adgeo-45-1-2018

Tadesse, B., Makuei, F., Albijanic, B., and Dyer, L. (2019). The beneficiation of lithium minerals from hard rock ores: a review. *Miner. Eng.* 131, 170–184. doi:10.1016/j.mineng.2018.

Tian, J., Xu, L., Wu, H., Fang, S., Deng, W., Peng, T., et al. (2018). A novel approach for flotation recovery of spodumene, mica and feldspar from a lithium pegmatite ore. *J. Clean. Prod.* 174, 625–633. doi:10.1016/j.jclepro.2017.10.331

USGS (2023). Mineral commodity 2022 summary: lithium.

Vera, M. L., Torres, W. R., Galli, C. I., Chagnes, A., and Flexer, V. (2023). Environmental impact of direct lithium extraction from brines. *Nat. Rev. Earth Environ.* 4, 149–165. doi:10.1038/s43017-022-00387-5

Vieceli, N., Nogueira, C. A., Pereira, M. F. C., Durão, F. O., Guimarães, C., and Margarido, F. (2018). Optimization of an innovative approach involving mechanical activation and acid digestion for the extraction of lithium from lepidolite. *Int. J. Minerals, Metallurgy Mater.* 25, 11–19. doi:10.1007/s12613-018-1541-7

WORLD BANK GROUP (2020). Minerals for climate action: the mineral intensity of the clean energy transition. Washington, D.C., United States: WORLD BANK GROUP

Yusupov, T. S., Isupov, V. P., Vladimirov, A. G., Zagorsky, V. E., Kirillova, E. A., Shumskaya, L. G., et al. (2015). Analysis of material composition and dissociation potential of minerals in mine waste to assess productivity of lithium concentrates. *J. Min. Sci.* 51, 1242–1247. doi:10.1134/s106273911506054x