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Assessment of a spodumene ore by advanced analytical and mass spectrometry techniques to determine its amenability to processing for the extraction of lithium

Mark G. Aylmore[a,*], Kelly Merigot[a], William D.A. Rickard[a,b], Noreen J. Evans[a,b,c], Bradley J. McDonald[a,c], Enej Catovic[d], Peter Spitalny[d]

[a] John de Laeter Centre, Faculty of Science & Engineering, Curtin University, Australia
[b] The Institute for Geoscience Research, Curtin University, Australia
[c] Department of Applied Geology, Curtin University, Australia
[d] Lithium Australia, Australia

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ABSTRACT

A combination of analytical microscopy and mass spectrometry techniques have been used to detect and characterise different lithium minerals in a LCT-Complex spodumene-type pegmatite from Pilgangoora located in the Pilbara region of Western Australia. Information collated by these techniques can be used to predict processing amenability. Samples were categorised into three subsamples (Pil1, Pil2, Pil3) based on colour and texture having different lithologies.

The mineralogy and liberation characteristics of samples were characterised using automated mineralogy techniques and the Li content and elemental distribution within minerals defined using instrumentation with secondary mass spectrometry capabilities. The majority of lithium is associated with spodumene particles with minor amounts of lithium bearing micas and beryl in the Pil1 sample, whereas in Pil2 and Pil3 spodumene is largely the lithium source. In the Pil1 sample a proportion of spodumene particles have undergone alteration with spodumene being replaced by micaceous minerals of muscovite, lepidolite and trilithionite, as well as calcite. In Pil2 and Pil3 samples the spodumene particles are generally free of mineral impurities except minor intergrowths of quartz, feldspar and spodumene are evident in the coarser fractions.

Based on mineralogical observations in the current study, the majority of the main gangue minerals quartz, K feldspar and albite can be rejected at a coarse grind size of −4 mm, to recover 90% of the spodumene with Li upgrade from 0.99–1.5 wt% Li to 3.0–3.5 wt% (6.5–7.5 wt% Li_2O). The iron content (81–1475 ppm) in the spodumene is low and therefore make these spodumene concentrates suitable for use in ceramic and glass applications.

Recovery of spodumene in the coarse fractions could be improved by further particle size reduction to liberate spodumene from micas and feldspars in the middling class, which account for between 15 and 49% of the sample. However, the requirement to remove mineral impurities in the spodumene in downstream processing will be dependent on the method of processing as the presence of Li bearing micas, calcite and feldspar can be beneficial or detrimental to lithium recovery.

The high content of Rb (1 wt%) and the abundance of free grains makes K feldspar a source of rubidium, particularly in the Pil3 sample which has K feldspar in high abundance (21 wt%) and can potentially be recovered by reverse flotation technique.

The low concentrations of the Ta, Nb and Sn minerals identified in samples were found to be fairly well liberated and could be recovered by conventional gravity separation techniques.

1. Introduction

The demand for lithium has increased significantly in recent years as a result of an increase in demand for lithium based rechargeable batteries for portable electronic devices (e.g. mobile phones, computers and rechargeable power tools) and electric passenger cars. Spodumene

* Corresponding author.
E-mail address: mark.aylmore@curtin.edu.au (M.G. Aylmore).

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(6.0–7.5% Li_2O) in high grade lithium-caesium-tantalum (LCT) pegmatite deposits is a major source of lithium. Other lithium minerals which are considered of commercial value are petalite (3.5–4.5% Li_2O), and the Li-bearing micas (polylithionite, trilithionite, lepidolite, zinnwaldite, which contain Li_2O ranging from 2.0 to 7.7%). Spodumene occurs naturally in the α monoclinic (C2/c) form as a member of the pyroxene group and found associated with quartz, albite, microcline and micas in pegmatite deposits. Pure stoichiometric chemical composition of spodumene consists of 8.0 wt.% Li_2O, 27.4 wt.% Al_2O_3 and 64.6 wt.% SiO_2. LCT pegmatites often contain high contents (> 0.9%) of rubidium and caesium which can also be recovered as byproducts.

Various processes have been developed and reported in the literature to recover lithium from Li-bearing minerals (Dresler et al., 1998; Distin and Phillips, 1982; Alex and Suri, 1996; Choubey, et al., 2016; Meshram, et al., 2014; Brandt and Haus, 2010). The key challenges associated with the beneficiation of lithium minerals has recently been discussed (Gibson et al., 2017). The processing of spodumene pegmatitic ores requires physical beneficiation which consists of grinding, sizing, flotation, gravity and/or heavy media/magnetic separation techniques to liberate and concentrate spodumene from gangue material. Spodumene is upgraded to make either chemical or ceramic grade concentrate. The type of concentrate is dependent on the impurities in the spodumene crystal lattice and the size distribution of particles. Therefore the beneficiation steps used to concentrate spodumene is very much dependent on the mineralogy.

The most common industrial processes for the extraction of lithium from spodumene requires the conversion of the α-spodumene form at elevated temperatures (1000–1100 °C) to the β-spodumene form to generate a porous material which is more amendable to either an acid or alkaline digestion for extraction of lithium and other elements, such as rubidium and caesium. Lithium can be recovered as a carbonate, hydroxide or chloride from the converted spodumene concentrate with sulfuric acid process (Garrett, 2004) or with sodium carbonate autoclave process (Chen et al., 2011; Olivier and Nenniger, 1979). Less energy intensive process options such as the halide based Sileach™ process are also being developed which may allow treatment of a wider range of lithium ore feeds (Griffin, 2017). However, the deportment of deleterious elements such as fluorine from micas can be problematic and important in considering process paths for treatment. In addition, the dissolution of other metals present in the ore, particularly Fe, Mn and Al, requires further purification steps to eliminate them.

In Australia, spodumene concentrates are produced and exported from pegmatite deposits at Greenbushes, Mt Cattlin and Mt Bald in Western Australia. Various companies are set to mine LCT-Complex spodumene-type pegmatites from Pilgangoora located in the Pilbara region of Western Australia. The potential production of Li from Pilgangoora's abundant pegmatites containing lepidolite and spodumene is considered a significant Li resource (Table 1).

To facilitate further process development, a comprehensive understanding of the deportment of lithium and associated minerals in potential ore bodies is essential to allow the industry to predict the response of ore reserves to metallurgical treatment options. Conventional chemical analytical and recent field ablation analysis techniques do not provide direct information about lithium deportment and the minerals associated with lithium. Furthermore, lithium is very difficult to analyse using conventional X-ray based techniques. In addition, publications using automated mineralogy to characterise Li-bearing ores, the deportment of Li and mineral textures have until recently been limited. (e.g., Grammatikopoulos et al., 2009; Sandmann and Gutzmer, 2013; Gibson et al., 2017).

This paper describes results from the integrated use of the John de Laeter Centre's analytical and mass spectrometry techniques to characterise Pilgangoora spodumene pegmatite ores. The mineralogical observations are then related to the processing properties of spodumene ores.

Table 1
LCT pegmatite deposit resource in the Pilbara craton (Taken from the Geology Survey of Western Australia, 2017).

Mining company	Ore (Mt)	Average Grade Li_2O (%)	Contained Li_2O (Mt)
Altura Mining Limited (Pilgangoora)	42.6	1.04	0.44
Pilbara Minerals (Pilgangoora)	150.6	1.24	1.86
Pilbara Minerals (Lynas Find)	5.60	1.57	0.09
Mineral resources (Wodgina)	140.9	1.24	1.75

2. Methodology

Mineral specimens of different Li minerals were collected from sites around Western Australia and first characterised using wet chemical and laser ablation ICPMS techniques to generate a mineral database. This database was then used to define and search for the minerals in Pilgangoora samples. A study on the Li bearing micas have been described elsewhere (Aylmore et al., 2018). For clarity a table of the minerals and average compositions used are present in Table 2. Lepidolite represents a solid solution series and intergrowths between the Al-bearing micas of polylithionite and trilithionite, whereas zinnwaldite is the Fe bearing micas ranging from trilithionite – polylithionite series to siderophyllite (Foster, 1960). The different Li-bearing micas and muscovite can be distinguished based on their aluminium and silica ratio as well as elemental impurities associated with them (Aylmore et al., 2018).

Of note is that, apart from the lithium content, many of these minerals contain elements such as Mn, Fe, Rb, F and Cs that can either be a by-product if in high concentration (e.g. Rb, Cs) or impinge on the method of processing (e.g. sulfate roasting of micas generating HF gas).

2.1. Ore samples

Samples were taken from outcrops of pegmatite within Pilbara Minerals Ltd Pilgangoora Project and collected by Lithium Australia NL and combined. The samples represent the spodumene zone lithologies within LCT-Complex spodumene-type pegmatites (Cerny and Ercit, 2005) that are part of the mineral resource that will be mined by Pilbara Minerals Ltd. Lithium Australia NL has a strategic alliance with Pilbara Minerals Ltd to assist the development of the halogen-based Sileach™ process, which can recover Li from spodumene without roasting. Pilbara Minerals is currently building a 2 Mtpa concentrate plant at Pilgangoora to produce a chemical grade 6 wt% Li_2O spodumene concentrate and a tantalite 30% Ta_2O_5 concentrate (Pilbara Minerals Ltd., 2017).

The combined sample was categorised into three subsamples based on the colour and texture. These subsamples were treated and characterised separately (Fig. 1).

2.2. Sample preparation

The samples were first crushed to pass a 3.5 cm screen size. They were then subjected to electrodynamic fragmentation (using SelFrag™) and screened to pass a 4 mm stainless-steel sieve. The electrodynamic fragmentation technique preserves the original crystal morphology and shape, crystal structure and physical and textural features, and allows the study of mineral in their nature form which is often sacrificed during grinding and milling. The electrodynamic fragmentation approach has been successfully used in both geological and metallurgical applications (e.g. Lastra and Cabri, 2003; Chernet, 2010; Wang et al., 2012; Sandmann & Gutzmer, 2013; Brandt & Haus, 2010; Aylmore et al., 2018).

Representative subsamples were split for detailed bulk