Accurate mineralogical analysis for lithium ore processing
Analyse minéralogique pour le traitement du minerai de lithium
Marie-Ève Provencher & Dr. Uwe König
Topics

Mineralogical monitoring of lithium ores

Motivation & value

Lithium deposits and processing

What is X-ray diffraction (XRD)

Case study - Pegmatites

Case study - Brines

Conclusions
Motivation and value

Mineralogical monitoring of lithium ores

• Increased demand for lithium

• Efficiency of lithium ore processing depends on mineralogical properties (not only on chemistry)

• Increased complexity of mineralogy of new and existing deposits
  • Exact knowledge of ore domains needed for efficient ore sorting and blending
  • Recovery rates and profitability of downstream processing requires exact knowledge of mineralogical composition
  • Efficient use of reagents
  • Minimum downtime
  • …
Increased demand for lithium

How much lithium is in everyday item?

- Tesla Model S: 51 kg
- Other Electric Vehicles: 10-63 kg
- Powerwall 2.0: 10 kg
- Hybrid Electric Vehicles: 0.8-2 kg

- Power Tool Batteries: 40-60 g
- Laptop Batteries: 30-40 g
- Tablet Batteries: 20-30 g
- Smartphone Batteries: 2-3 g

Source: [www.visualcapitalist.com](http://www.visualcapitalist.com)
Increased demand for lithium

Forecast consumption

Forecast consumption of lithium by first use, 2016-2031 (000t LCE)

Source: Roskill Consulting Group Ltd, 2017
Sources: USGS (2017), producer announcements
Lithium deposits
Lithium deposits

Overview

- IGNEOUS
  - 138 Li deposits
  - 66 resources
  - 20.8 Mt Li (23.1 Mt Li eq.)

- PEGMATITE
  - 125 Li deposits
  - 60 resources
  - 18.8 Mt Li (20.1 Mt Li eq.)

- VOLCANIC SEDIMENT-HOSTED
  - 8 Li deposits
  - 2 resources
  - 1.0 Mt Li (1.2 Mt Li eq.)

- LI-RICH CLAY
  - 4 Li deposits

- B-RICH CLAY
  - 4 Li deposits

- U-RICH CLAY
  - 1 Li deposit

- SEDIMENTARY
  - 37 Li deposits
  - 10 resources
  - 7.9 Mt Li (8.8 Mt Li eq.)

- BRINE (SALAR / SALT LAKE)
  - 170 Li deposits
  - 27 resources
  - 31.1 Mt Li (57.0 Mt Li eq.)

- UNCONVENTIONAL BRINE
  - 44 Li deposits
  - 9 resources
  - 13.6 Mt Li (17.6 Mt Li eq.)

- OILFIELD BRINE
  - 35 Li deposits
  - 8 resources
  - 10.7 Mt Li (14.6 Mt Li eq.)

- GEOTHERMAL BRINE
  - 9 Li deposits
  - 1 resource
  - 2.8 Mt Li (3.0 Mt Li eq.)

NB: the 'unconventional' deposits are technically a sub-category of brine deposits, but have been listed separately in this framework to differentiate between technically feasible (‘salar’) and not yet technically feasible (unconventional) deposits.

Sykes - MinExConsulting, 2019
Lithium deposits

Brines versus pegmatites

- Formed by leaching of volcanic rocks in basin depositional environments
- **Large low-grade deposits**
  - Extraction of Li involving the pumping of brine, concentration via evaporation, and purification through solvent extraction, end product mainly \( \text{Li}_2\text{CO}_3 \)

- Lithium-bearing, aluminium silicate mineral which mostly occurs in lithium-rich pegmatites (granite-like igneous rock composed of quartz, feldspar and mica).
- **Complex high-grade deposits**
  - Spodumene usually recovered through open pit mining
  - Beneficiated via gravity techniques where the ore is concentrated from 1-2% \( \text{Li}_2\text{O} \) to a grade of ~6% \( \text{Li}_2\text{O} \)
Lithium deposits
Brines versus pegmatites

'Unconventional' deposits are a sub-group of brine deposits that are not yet technically feasible.
Lithium deposits

Costs

Reagent and royalty costs contribute almost 60% of brine operations' total cash costs.

Data as of May 6, 2019.
Source: S&P Global Market Intelligence
X-ray diffraction (XRD)
Analytical techniques
Elements and minerals

<table>
<thead>
<tr>
<th>Wet chemistry</th>
<th>XRF</th>
<th>Neutron analysis</th>
</tr>
</thead>
</table>

| Elements | | | |
|----------|-------------------|
| Fe | SiO2 | Al2O3 | MgO | CaO | S |
| 1 | 26.5 | 22.2 | 0.4 | 17.9 | 2.1 | 4.0 |
| 2 | 57.9 | 6.1 | 0.8 | 3.9 | 1.9 | 4.9 |
| 3 | 34.5 | 23.1 | 2.0 | 12.5 | 4.4 | 2.1 |

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Process parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyr</td>
<td>Mag</td>
</tr>
</tbody>
</table>

| XRD | NIR | Electron microprobe | MLA, QEMSCAN | Microscopy |
XRD in Geoscience

Usage

Main fields of applications:

- Research
- Exploration
- Processing
- Environment
XRD in Geoscience
What can we learn from XRD pattern?

- Phase composition
- Amorphous content
- Crystallite size/microstrain
- Structural information
- Process parameters
X-ray diffraction

How does it work?

- Identification and quantification of crystalline phases and amorphous content
- Monitoring of process parameters
X-ray diffraction
Data evaluation

Calibration

Rietveld

- Barite 22.9%
- Hematite, syn 21.8%
- Quartz 5.9%
- Goethite 29.7%
- Fluorapatite, syn 5.3%
- Synchysite-(Ce) 2.7%
- Duplicated_Barite 11.6%
X-ray diffraction

Data evaluation

Calibration  PLSR
Partial Least Squares Regression

Rietveld  Clustering
Similarity analysis

<table>
<thead>
<tr>
<th>Position [°2Theta] (Copper (Cu))</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>10000</td>
</tr>
<tr>
<td>30</td>
<td>20000</td>
</tr>
<tr>
<td>40</td>
<td>30000</td>
</tr>
<tr>
<td>50</td>
<td>40000</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
</tr>
</tbody>
</table>

Barite 22.9 %
Hematite, syn 21.8 %
Quartz 5.9 %
Goethite 29.7 %
Fluorapatite, syn 5.3 %
Synchysite-(Ce) 2.7 %
Duplicated Barite 11.6 %
Case study: Pegmatites
Pegmatite ores

Process

Spodumene concentrate

High purity lithium carbonate (≥ 99.5%)

Filtration

Analcime

Crushing → Separation → Grinding → Rotation → Dewatering → Filtration → Pressure leaching and hydrocarbonation in alkaline media → Dewatering → Impurity ion exchange → Crystallization → Filtration → Analcime

Spodumene ore
Process

Pegmatite ores

Samples case study
Mineralogical monitoring…

**Exploration, mine planning, process monitoring**

- Samples from several parts during mining and processing of lithium ores were analyzed
  - Lithium **ore** (raw material)
  - **Concentrate** (α – Spodumene)
  - Flotation **tailings**
  - **Calcination** product (β – Spodumene)
  - **Residue** (Analcime)

- Sample preparation
  - Automatic mill / press combination to ensure minimum sample preparation errors

- Measurement time per sample **8 min** (Aeris Minerals, benchtop XRD)
Cluster analysis
Lithium ores

- Prior to phase identification and quantification a **cluster analysis** was performed using all available ore samples
- 2 cluster (groups of similar samples) are identified
- 2 outliers (not belonging to any cluster)
- → fast check for different ore domains for greenfield or brownfield exploration
Lithium containing minerals

Pegmatites

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Theoretical Li Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spodumene</td>
<td>LiAlSi$_2$O$_6$</td>
<td>3.73</td>
</tr>
<tr>
<td>Petalite</td>
<td>LiAlSi$<em>4$O$</em>{10}$</td>
<td>2.27</td>
</tr>
<tr>
<td>Eucryptite</td>
<td>LiAlSiO$_4$</td>
<td>5.51</td>
</tr>
<tr>
<td>Bikitaite</td>
<td>LiAlSi$_2$O$_6$.H$_2$O</td>
<td>3.40</td>
</tr>
<tr>
<td>Lepidolite</td>
<td>KL$_2$AlSi$<em>3$O$</em>{10}$(OH,F)$_2$</td>
<td>~3.84</td>
</tr>
<tr>
<td>Zinnwaldite</td>
<td>KLFeAl$_2$Si$<em>3$O$</em>{10}$(F,OH)$_2$</td>
<td>1.59</td>
</tr>
<tr>
<td>Amblygonite</td>
<td>(Li,Na)AlPO$_4$(OH,F)</td>
<td>4.73</td>
</tr>
<tr>
<td>Montebrasite</td>
<td>LiAl(PO$_4$)(OH)</td>
<td>1 to 4</td>
</tr>
<tr>
<td>Lithiophylite</td>
<td>LiMnPO$_4$</td>
<td>4.43</td>
</tr>
<tr>
<td>Triphyllite</td>
<td>LiFePO$_4$</td>
<td>4.40</td>
</tr>
<tr>
<td>Hectorite</td>
<td>Na$_{0.3}$(Mg,Li)$_3$Si$<em>4$O$</em>{10}$(OH)$_2$</td>
<td>~1.93</td>
</tr>
<tr>
<td>Jadarite</td>
<td>LiNaAlSi$_2$O$_7$(OH)</td>
<td>2.85</td>
</tr>
<tr>
<td>Zabuyelite</td>
<td>Li$_2$CO$_3$</td>
<td>18.79</td>
</tr>
<tr>
<td>Elbaite</td>
<td>Na(Li$<em>{1.5}$Al$</em>{1.5}$)Al$_6$Si$_6$B$<em>3$O$</em>{27}$(OH)$_4$</td>
<td>1.11</td>
</tr>
</tbody>
</table>

- Spodumene theoretically contains 8.03% Li$_2$O
Lithium containing minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Theoretical Li Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spodumene</td>
<td>LiAlSi$_2$O$_6$</td>
<td>3.73</td>
</tr>
<tr>
<td>Petalite</td>
<td>LiAlSi$<em>4$O$</em>{10}$</td>
<td>2.27</td>
</tr>
<tr>
<td>Eucryptite</td>
<td>LiAlSiO$_4$</td>
<td>5.51</td>
</tr>
<tr>
<td>Bikitaite</td>
<td>LiAlSi$_2$O$_6$.H$_2$O</td>
<td>3.40</td>
</tr>
<tr>
<td>Lepidolite</td>
<td>KLi$_2$AlSi$<em>3$O$</em>{10}$(OH,F)$_2$</td>
<td>~3.84</td>
</tr>
<tr>
<td>Zinnwaldite</td>
<td>KLiFeAl$_2$Si$<em>3$O$</em>{10}$(F,OH)$_2$</td>
<td>1.59</td>
</tr>
<tr>
<td>Amblygonite</td>
<td>(Li,Na)AlPO$_4$(OH,F)</td>
<td>4.73</td>
</tr>
<tr>
<td>Montebrasite</td>
<td>LiAl(PO$_4$)(OH)</td>
<td>1 to 4</td>
</tr>
<tr>
<td>Lithiophylite</td>
<td>LiMnPO$_4$</td>
<td>4.43</td>
</tr>
<tr>
<td>Triphylite</td>
<td>LiFePO$_4$</td>
<td>4.40</td>
</tr>
<tr>
<td>Hectorite</td>
<td>Na$_{0.3}$(Mg,Li)$_3$Si$<em>4$O$</em>{10}$(OH)$_2$</td>
<td>~1.93</td>
</tr>
<tr>
<td>Jadarite</td>
<td>LiNaAlSi$_2$O$_7$(OH)</td>
<td>2.85</td>
</tr>
<tr>
<td>Zabuyelite</td>
<td>Li$_2$CO$_3$</td>
<td>18.79</td>
</tr>
<tr>
<td>Elbaite</td>
<td>Na(Li$<em>{1.5}$Al$</em>{1.5}$)Al$_6$Si$_6$B$<em>3$O$</em>{22}$(OH)$_4$</td>
<td>1.11</td>
</tr>
</tbody>
</table>

- Spodumene theoretically contains 8.03% Li$_2$O
Mineralogy
Phase identification pegmatites

- Complex mineralogy
- 8 main and minor minerals identified in the lithium ores
- Additional mineral phases identifies in the processed ore
- XRD can distinguish between α- and β-spodumene !!!
### Mineralogy

#### Phase identification

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spodumene</td>
<td>LiAl(SiO$_3$)$_2$</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi$_3$O$_8$</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl$_2$Si$_2$O$_8$</td>
</tr>
<tr>
<td>Lepidolite</td>
<td>K(Li,Al)$_3$(Al, Si, Rb)$<em>4$O$</em>{10}$(F, OH)$_2$</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>KAlSi$_3$O$_8$</td>
</tr>
<tr>
<td>Tourmaline (Elbaite)</td>
<td>Na(Li$<em>{1.5}$Al$</em>{1.5}$)Al$_6$Si$<em>6$O$</em>{18}$ (BO$_3$)$_3$(OH)$_4$</td>
</tr>
<tr>
<td>Beryl</td>
<td>Be$_3$Al$_2$(SiO$_3$)$_6$</td>
</tr>
</tbody>
</table>

- Complex mineralogy
- 8 main and minor minerals identified in the lithium ores
- Additional mineral phases identifies in the processed ore
- XRD can distinguish between α- and β-spodumene !!!
Mineralogy (quantification)

Lithium ores

Counts

- Spodumene-alpha 26.5%
- Spodumene-beta 0.0%
- Quartz 23.2%
- Albite 40.4%
- Anorthite 6.7%
- Orthoclase 0.4%
- Lepidolite 2.0%
- Beryl 0.7%
- Elbaite 0.0%
- Analcime 0.0%

Measurement time 8 min

Example of a full-pattern Rietveld quantification of a hard-rock lithium ore

Rwp = 10.1269
Mineralogy (quantification)

Processed lithium ore

Example of a full-pattern Rietveld quantification of a spodumene concentrate

Counts

Position [°2θ] (Copper (Cu))

Counts

Rwp = 9.4128
Results

Mineralogical monitoring pegmatite processing

Clustering
Results

Mineralogical monitoring pegmatite processing

Clustering

Mineral composition
Results

Mineralogical monitoring pegmatite processing

Clustering

Mineral composition

Grade blocks
Case study: Brines
Process Brines

Natural brines from El Salar ~ 0.16% Li

END BRINE 6.0% Li

Li$_2$CO$_3$ LiCl

Further Purification, Processing, Crystallization

NaCl + CaSO$_4$ * H$_2$O HALITE
NaCl + KCl SYLVINITE
MgCl$_2$ * KCl * 6H$_2$O CARNALLITE
MgCl$_2$ * 6H$_2$O BISCHOFITE
MgCl$_2$ * LiCl * 7H$_2$O Li CARNALLITE

Haber, LSM Conference, Las Vegas, 26-28th January 2010
Cluster analysis

Brine samples

- Halite > Sylvine
- Sylvine >> Halite
- Halite >> Sylvine
- Gypsum
- Carnalite
- Bischofite
- Lithium salts
Mineralogy
Phase identification brines

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halite</td>
<td>NaCl</td>
</tr>
<tr>
<td>Sylvine</td>
<td>KCl</td>
</tr>
<tr>
<td>Carnallite</td>
<td>KMgCl₃ · 6H₂O</td>
</tr>
<tr>
<td>Bischofite</td>
<td>MgCl₂ · 6H₂O</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄ · 2H₂O</td>
</tr>
<tr>
<td>Kainite</td>
<td>KMg(Cl,SO₄) · 2.75H₂O</td>
</tr>
<tr>
<td>Li-sulfate</td>
<td>Li₂SO₄ · H₂O</td>
</tr>
<tr>
<td>monohydrate</td>
<td></td>
</tr>
<tr>
<td>Li-Carnallite</td>
<td>LiMgCl₃ · 7H₂O</td>
</tr>
</tbody>
</table>
Mineralogy (quantification)

Lithium brines

Counts

- Halite 27.3 %
- Sylvine 11.0 %
- Carnallite, syn 45.8 %
- Chloromagnesite 0.5 %
- Anhydrite 1.6 %
- Picromerite, syn 1.0 %
- Polyhalite 10.1 %
- Lithium Sulfate Monohydrate 1.1 %
- Lithium Chloride Magnesium Dichloride Heptahydrate 1.6 %

Position [°2Theta] (Copper (Cu))
Conclusions
Conclusions

Mineralogical monitoring of lithium ores and brines

- Fast tool to monitoring qualitative and quantitative mineral composition of lithium ore
- Fast detection of impurities or off-spec ore mineralogy
- BT XRD in laboratories or containers or an automated environment

- Fast decision making and counteractions on changing conditions, reduced operational costs
- Additional information for mine planning and downstream processing
- Higher degree of process automation with less manual testing, improved safety, lowest energy costs
Questions?

Marie-Ève Provencher
marie.eve.provencher@malvernpanalytical.com

Dr. Uwe König
uwe.koenig@malvernpanalytical.com

www.malvernpanalytical.com