The challenges of Li determination in minerals: A comparison of stoichiometrically determined Li by EPMA with direct measurement by LA-ICP-MS and handheld LIBS

Robin Armstrong (NHM)
THE TEAM & ACKNOWLEDGEMENTS

• This work was carried out as part of the WP2 of the FAME project

• The “analysts”: John Spratt & Yannick Buret (NHM) and Andrew Somers (SciAps)

• The “mineralogists”: Fernando Noronha & Violeta Ramos (UP), Mario Machado Leite (LNEG), Jens Anderson, Beth Simmons & Gavyn Rollinson (CSM), Chris Stanley, Alla Dolgopolova, Reimar Seltmann & Mike Rumsey* (NHM)

• Literature mineral data is taken from Mindat, Webmineral and DHZ

• Robin Armstrong (R.Armstrong@nhm.ac.uk)
INTRODUCTION

• The analytical problems of Li
  • Whole Rock analysis (WR)
    • Examples and is it safe to make mineralogical assumptions on the base of WR
  • Li Mineral analysis
    • Li-minerals overview
    • Li-minerals examined
    • EPMA
    • LA-ICP-MS
    • LIBS
  • Summary and thoughts for the future
LITHIUM ORES ARE POTENTIALLY COMPLEX

- Li-bearing phases identified:
  - Lepidolite
  - Amblygonite-Montebrasite group
  - Lithiophosphate(tr) and Petalite

\[ \text{Li} = 1.17 \text{ wt\%} \]
WHOLE ROCK ANALYSIS (Li ASSAYS)

• Li is not that straightforward to analyse in whole rock
  • Its low mass means that there are low fluorescence yields and long wave-length characteristic radiation rule out lab-based XRF and pXRF
  • We cannot use conventional fluxes as these are generally Li-based
  • We can use “older” non Li fluxes such as Na₂O₂ but then there maybe contamination issues in the instruments
  • We can use multi-acid digests (HF+HNO₃+HClO₄ digestion with HCl-leach) (FAME used the ALS ME-MS61) however there may still be contamination issues and potentially incomplete digestion.

• It has been noted that the comparability between methods is sometimes poor (>10% difference)
COMPARISON OF METHODS: AN EXAMPLE

• Samples from the Kaustinen area spodumene pegmatites supplied to the FAME project by Keliber Oy Finland.

• 4 acid digestion vs Na$_2$O$_2$ flux then acid – both with ICP-AES finish

<table>
<thead>
<tr>
<th>4 Acid Li ppm</th>
<th>Na$_2$O$_2$ Li ppm</th>
<th>%diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>7410</td>
<td>8300</td>
<td>11.33</td>
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<td>5610</td>
<td>6860</td>
<td>20.04</td>
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<td>7870</td>
<td>8640</td>
<td>9.33</td>
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<td>1180</td>
<td>1380</td>
<td>15.62</td>
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<tr>
<td>5910</td>
<td>6640</td>
<td>11.63</td>
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<tr>
<td>4390</td>
<td>4820</td>
<td>9.34</td>
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<tr>
<td>5400</td>
<td>6160</td>
<td>13.15</td>
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</table>
WHAT CAN WR DATA TELL US?

- Going to take 3 sets of whole rock data from the FAME project
- Keliber’s Kaustinen area spodumene pegmatites
- Gonçalo pegmatite/ aplite field – lepidolite, petalite & Li-phosphates
- Cinovec greisens – Li-micas
- All data generated at ALS-global, QAQC runs at NHM
KAUSTINEN AREA - SPODUMENITE

Graph showing the relationship between K/Al and Li_M, with different sample types represented by color-coded lines and markers.
GONÇALO – LEPIDOLITE / Li-PHOSPHATES

[Graph showing data points and lines for Lithium Aluminosilicates and Lithophosphates]

- P_M vs Li_M
- K/Al vs Li/Al

Legend:
- ○ Gonçalo
- → Li-Al-PO4
- → Lithiophosphate
- → Li/Al
- → Lepidolite
- → Zinnwaldite
- → Muscovite
- → Spodumene
CINOVEC – Li-MICAS
• The pre-digestion prep has to be good (fine grind)
• Choose your digestions and finishes carefully
• You can use molar proportions to mineralogically “play data”
• For the Li–minerals appears to work better at higher Li assay values

• Bear in mind that most of the “main” Li-bearing phases are variations on the theme of $\text{Li}\pm\text{Al}\pm\text{Si}\pm\text{K}\pm\text{Na}\pm\text{Fe}\pm\text{P}$

• If you want to understand Li deportment in the rock mass you need to do some petrography and mineral chemistry.
## LITHIUM MINERALS (IMA – APPROVED*)

<table>
<thead>
<tr>
<th>Aleksandrovite</th>
<th>Amblygonite</th>
<th>Balestraite</th>
<th>Balipholite</th>
<th>Baratovite</th>
<th>Berezanskite</th>
<th>Bertossaite</th>
<th>Bikitaite</th>
<th>Bityite</th>
<th>Borocookeite</th>
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<tbody>
<tr>
<td>Brannockite</td>
<td>Bulgakite</td>
<td>Clino-ferri-holmquistite</td>
<td>Clino-ferri-ferri-holmquistite</td>
<td>Colquirite</td>
<td>Cookeite</td>
<td>Cryolithinite</td>
<td>Darapiosite</td>
<td>Dusmatovite</td>
<td>Darrellhenryte</td>
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<td>Elbaite</td>
<td>Eliseevite</td>
<td>Emeleusite</td>
<td>Ephesite</td>
<td><strong>Eucryptite</strong></td>
<td>Faizievite</td>
<td>Ferri-fluoro-leakeite</td>
<td>Ferri-leakeite</td>
<td>Ferrisicklerite</td>
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<td>Ferro-ferri-pedrizite</td>
<td>Ferro-holmquistite</td>
<td>Ferro-pedrizite</td>
<td>Fluor-elaite</td>
<td>Fluor-liddicoatite</td>
<td>Fluoro-leakeite</td>
<td>Gainesite</td>
<td>Garnite</td>
<td>Gorbunovite</td>
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<td>Grighite</td>
<td>Hectorite</td>
<td>Holmquistite</td>
<td>Hsianghualite</td>
<td><strong>Jadarkite</strong></td>
<td>Katayamalite</td>
<td>Lavinskyite</td>
<td>Liberite</td>
<td>Lintsize</td>
<td>Lithiomarsturite</td>
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<td>Lithiophilithe</td>
<td>Lithiophorite</td>
<td>Lithiophosphate</td>
<td>Lithioantlite</td>
<td>Lithiowodginite</td>
<td>Luanshiweite</td>
<td>Lunijianlite</td>
<td>Magnesio-Neptunite</td>
<td>Magnesiostaurolite</td>
<td>Manandonite</td>
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<td>Mangana-Delaventurate</td>
<td>Manganoneunite</td>
<td>Masatomilite</td>
<td>Mccrillisite</td>
<td><strong>Montebasite</strong></td>
<td>Murakamiite</td>
<td>Nalipoite</td>
<td>Nalivkinite</td>
<td>Nambulite</td>
<td>Nanlingite</td>
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<tr>
<td>Natronambulate</td>
<td>Neptunite</td>
<td>Norrishite</td>
<td>Olympite</td>
<td>Orlovite</td>
<td>Oxo-mangani-leakeite</td>
<td>Pahasapait</td>
<td>Palermoite</td>
<td>Peatite-(Y)</td>
<td><strong>Petalite</strong></td>
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<tr>
<td>Sicklerite</td>
<td>Silinaite</td>
<td>Simferite</td>
<td>Simmonsite</td>
<td>Sogdianite</td>
<td>Sokolovaite</td>
<td><strong>Spodumene</strong></td>
<td>Sugilite</td>
<td>Swinefordite</td>
<td>Tainiolite</td>
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<td>Tancoite</td>
<td>Tanohataite</td>
<td>Tavorite</td>
<td>Tiptopite</td>
<td>Trilithionite</td>
<td>Triphylite</td>
<td>Virgilite</td>
<td>Voloshinite</td>
<td>Walkerite</td>
<td>Watatsumiite</td>
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<td>Wilanookite</td>
<td>Zabuyelite</td>
<td>Zektzerite</td>
<td><strong>Lepidolite</strong></td>
<td>Zinnwaldite</td>
<td>Li-muscovite</td>
<td>Li-phengite</td>
<td></td>
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*IMA - International Mineralogical Association
## MINERALS EXAMINED

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Li (wt%)</th>
<th>Dana Class</th>
<th>Hardness</th>
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<tbody>
<tr>
<td>Spodumene</td>
<td>LiAlSi$_2$O$_6$</td>
<td>3.73</td>
<td>Inosilicate (Pyroxene)</td>
<td>6.5-7</td>
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<tr>
<td>Eucryptite</td>
<td>LiAlSiO$_4$</td>
<td>5.51</td>
<td>Nesosilicate (Phenakite group)</td>
<td>6.5</td>
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<tr>
<td>Petalite</td>
<td>LiAl(Si$<em>4$O$</em>{10}$)</td>
<td>2.09</td>
<td>Phyllosilicate</td>
<td>6.5</td>
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<tr>
<td>Montebrasite</td>
<td>LiAl(PO$_4$)(OH)</td>
<td>4.74</td>
<td>Anhydrous Phosphates (Amblygonite Group)</td>
<td>5.5-6</td>
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<tr>
<td>Lithiophosphate</td>
<td>Li$_3$PO$_4$</td>
<td>17.98</td>
<td>Anhydrous Phosphates (Lithiophosphate Group)</td>
<td>4</td>
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<td>Hectorite</td>
<td>Na$_{0.3}$(Mg,Li)$_3$(Si$<em>4$O$</em>{10}$)(F,OH)$_2$</td>
<td>0.54</td>
<td>Phyllosilicate (Smectite group)</td>
<td>1-2</td>
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<tr>
<td>Lepidolite</td>
<td>KLi$<em>2$Al(Si$<em>4$O$</em>{10}$)(F,OH)$<em>2$ to K(Li$</em>{1.5}$Al$</em>{1.5}$)(AlSi$<em>3$O$</em>{10}$)(F,OH)$_2$</td>
<td>3.58</td>
<td>Phyllosilicate (Mica group)</td>
<td>2.5-3.5</td>
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<tr>
<td>Jadarite</td>
<td>LiNaSiB$_3$O$_7$OH</td>
<td>3.38</td>
<td>Nesosilicate (Howlite and related species)</td>
<td>4 - 5</td>
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<tr>
<td>Bityite</td>
<td>CaLiAl$_2$(AlBeSi$<em>2$)O$</em>{10}$(OH)$_2$</td>
<td>1.79</td>
<td>Phyllosilicate (Mica group)</td>
<td>5.5</td>
</tr>
</tbody>
</table>
ELECTRON BEAM TECHNIQUES AND Li-MINERALS

• Li minerals are difficult to analysis by electron beam techniques.

• Li’s mass too low for most detectors, therefore all but “invisible”

• Frequently accompanied by other problematic elements: O, H, Be, B, Rb & Cs....
WORKING ROUND THESE PROBLEMS

• Good optical assessment first, if the phases are present in the sufficient quantities employ XRD (has its own problems)
• Use of stoichiometric recalculations, some minerals are easier than others
• Even if you cannot detect it, Analytical SEM techniques provide valuable textural information on phase distribution and intergrowths
• Use of elemental ratios in combination (this approach has reasonable success with QEM scan)
THERE DO EXISTS PROTOCOLS FOR PARTICULAR MINERALS USING EPMA

• For example:
  • Tischendorf, Forster & Gottesmann (1999) for estimation of Li in trioctahedral micas (Mg)
  • Tindle & Webb (1990) estimation of Li in trioctahedral micas (Si)
### EPMA – ANALYTICAL CONDITIONS

<table>
<thead>
<tr>
<th>Sp</th>
<th>Elements</th>
<th>X-ray line</th>
<th>Xtal</th>
<th>Time (S)</th>
<th>DLS (ppm)</th>
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<td>Sp2</td>
<td>F</td>
<td>Kα</td>
<td>LPC0</td>
<td>30</td>
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<td>TAP</td>
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<td>261</td>
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<td>Cl</td>
<td>Kα</td>
<td>PET</td>
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<td>426</td>
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<tr>
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<td>K</td>
<td>Kα</td>
<td>LPET</td>
<td>10</td>
<td>209</td>
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<tr>
<td>Sp1</td>
<td>Ca</td>
<td>Kα</td>
<td>PET</td>
<td>30</td>
<td>169</td>
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<td>Sp5</td>
<td>Mn</td>
<td>Kα</td>
<td>LLIF</td>
<td>20</td>
<td>248</td>
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<td>Sp5</td>
<td>Fe</td>
<td>Kα</td>
<td>LLIF</td>
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<td>Rb</td>
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<td>LLIF</td>
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<td>Ti</td>
<td>Kα</td>
<td>LPET</td>
<td>20</td>
<td>148</td>
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<td>Sr</td>
<td>Lα</td>
<td>LPET</td>
<td>30</td>
<td>606</td>
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<td>Sp3</td>
<td>Cs</td>
<td>Lα</td>
<td>LPET</td>
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<td>Sp1</td>
<td>Ba</td>
<td>Lα</td>
<td>PET</td>
<td>20</td>
<td>776</td>
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</table>

- **CAMECA SX100**
- **Natural History Museum**
- **Beam current 20nA**
- **Accelerating voltage 20kV**
- **Spot size 3µm**
• Average Li (wt%) = 3.74
• Literature Li (wt%) = 3.73
LITHIOPHOSPHATE

- Average Li (wt%) = 18.88
- Literature Li (wt%) = 17.98
LEPIDOLITE

- Average Li (wt%) = 2.67
- Literature Li (wt%) = 3.73
JADARITE

• Average Li (wt%) = 3.18
• Literature Li (wt%) = 3.38%
LA-ICP-MS – ANALYTICAL CONDITIONS

Analytical conditions are:

- Fluence: 3.5 J/cm²
- Frequency: 5 Hz
- Spot size: 35 µm
- Gas flows:
  - He: ~0.7 L/min
  - Ar: ~1.1 L/min

New Wave 193nm excimer laser linked to an Agilent 7700 quadrupole ICP-MS

- Natural History Museum, LODE Lab
- Primary Standard NIST 610
- The element list was extensive....
- Included Li, B, Be
COMPARING Li VALUES: LA-ICP-MS VS EPMA

• The majority of the minerals have a good analytical agreement between the methods
• Lithiophosphate is significantly different
• Bityite is significantly different
• Hectorite is variable
• Jadarite is variable
LA-ICP-MS VS EPMA CONTINUED

- Bityite
- Hectorite
LIBS (Laser Induced Breakdown Spectroscopy)

- Optical Atomic Emission Spectroscopy (OES)
- Focused laser ablates surface to create a plasma
- Light from plasma is collected, run through a spectrometer and projected onto the detector creating a spectrum (x – wavelength, y – intensity)
SciAps Z300 Hand Held LIBS Spectra: 190-950nm
Li peaks used for direct measurement

LIBS Spectra

Wavelength (nm)

Signal

Intensity

Wavelength (nm)
**Lepidolite**

KLi2Al(Si4O10)(F,OH)2  to  K(Li1.5Al1.5)(AlSi3O10)(F,OH)2

K 766.49nm  Li 670.79nm  Al 396.152nm  Si 288.158nm  Na

---

**Comparison of results using different analytical techniques**

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>Al</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIBS</td>
<td>3.1602</td>
<td>0.0003</td>
<td>10.898</td>
<td>11.5469</td>
<td>0.5623</td>
<td>18.2149</td>
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<tr>
<td>LA ICP MS</td>
<td>2.5968</td>
<td>0.002682</td>
<td>Not analysed</td>
<td>21.497</td>
<td>0.18733</td>
<td>8.5802</td>
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<tr>
<td>EPMA</td>
<td>1.4496*</td>
<td>Not analysed</td>
<td>12.2313</td>
<td>22.5672</td>
<td>0.2557</td>
<td>8.7195</td>
</tr>
</tbody>
</table>

*Not analysed but calculated by difference

*Rb by LA ICP-MS=0.8227%
**Bityite**

\[ \text{CaLiAl}_2(\text{AlBeSi}_2)\text{O}_{10}(\text{OH})_2 \]

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**Comparison of results using different analytical techniques**

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>Al</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
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</thead>
<tbody>
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<td><strong>LIBS</strong></td>
<td>1.4496</td>
<td>0.0002</td>
<td>10.4426</td>
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<td>-0.0403</td>
<td>4.488</td>
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<td><strong>LA ICP MS</strong></td>
<td>0.7366</td>
<td>0.001122</td>
<td>Not analysed</td>
<td>10.471</td>
<td>0.030534</td>
<td>0.95056</td>
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<tr>
<td><strong>EPMA</strong></td>
<td>3.1014*</td>
<td>Not analysed</td>
<td>14.6695</td>
<td>30.3558</td>
<td>0.0912</td>
<td>0.0035</td>
<td>-0.0015</td>
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</table>

* Not analysed but calculated by difference

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27th July, 2017

Drilling for Geology II, Brisbane, QLD, Australia
SUMMARY AND THOUGHTS

• Be cautious how you obtain assay data (consider a few repeats using different dissolutions)
• You can use WR data to predict the phases present
• The recalculation of Li values from EPMA data using stoichiometry for the most part corresponds to the direct measurement of Li by LA-ICP-MS
• There is a reasonable correlation of the LIBS data to the EPMA and ICP-MS data (considering the spatial sampling differences)
• We are now in a situation where we can proceed with a workflow for the more accurate deportment of Li in potential ores.