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

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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)

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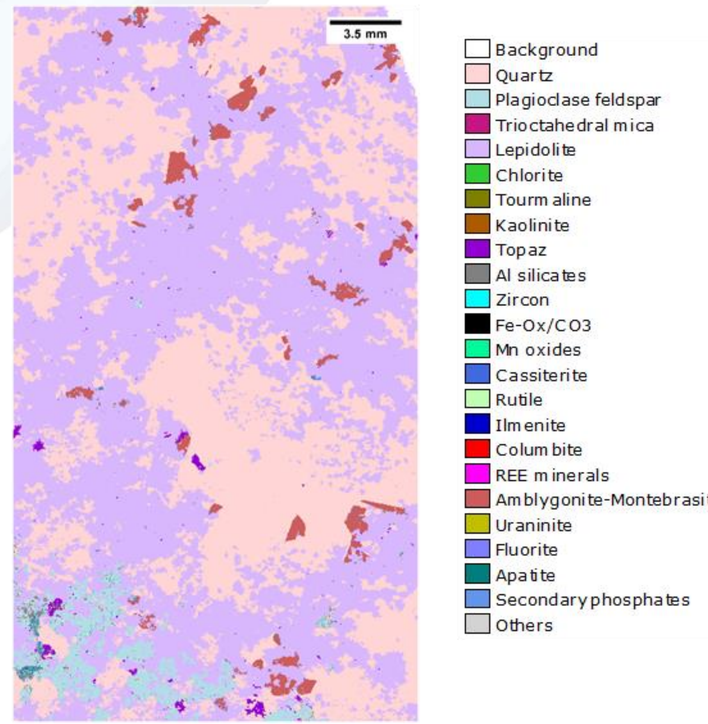
INTRODUCTION

- 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 = 1.17 wt%



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

WHOLE ROCK ANALYSIS (Li ASSAYS)

- Li is not that straight forward 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 Na_2O_2 but then there maybe contamination issues in the instruments
  - We can use multi-acid digests (HF+HNO_3+$HClO_4$ 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)

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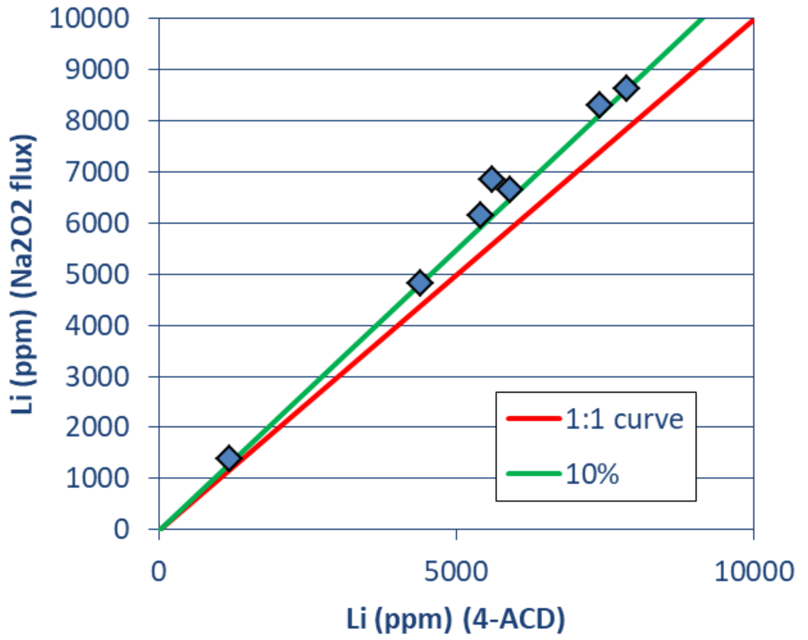
COMPARISON OF METHODS: AN EXAMPLE

- Samples from the Kaustinen area spodumene pegmatites supplied to the FAME project by Keliber Oy Finland.
- 4 acid digestion vs Na_2O_2 flux then acid – both with ICP-AES finish



4 Acid	Na_2O_2	
Li ppm	Li ppm	%diff
7410	8300	11.33036
5610	6860	20.04812
7870	8640	9.32768
1180	1380	15.625
5910	6640	11.63347
4390	4820	9.337676
5400	6160	13.14879

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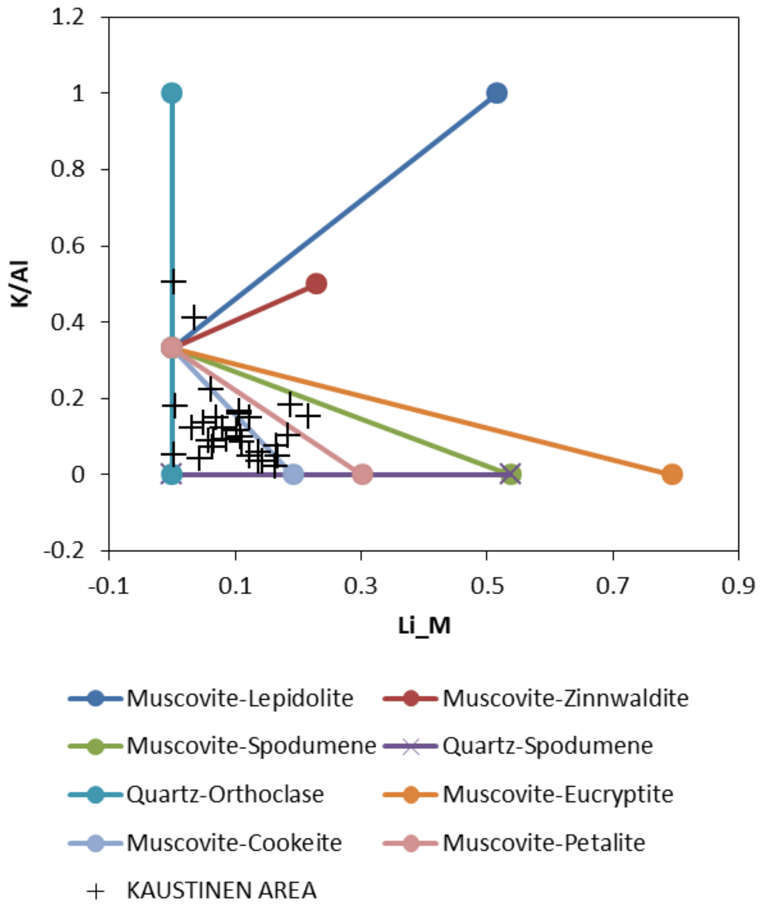
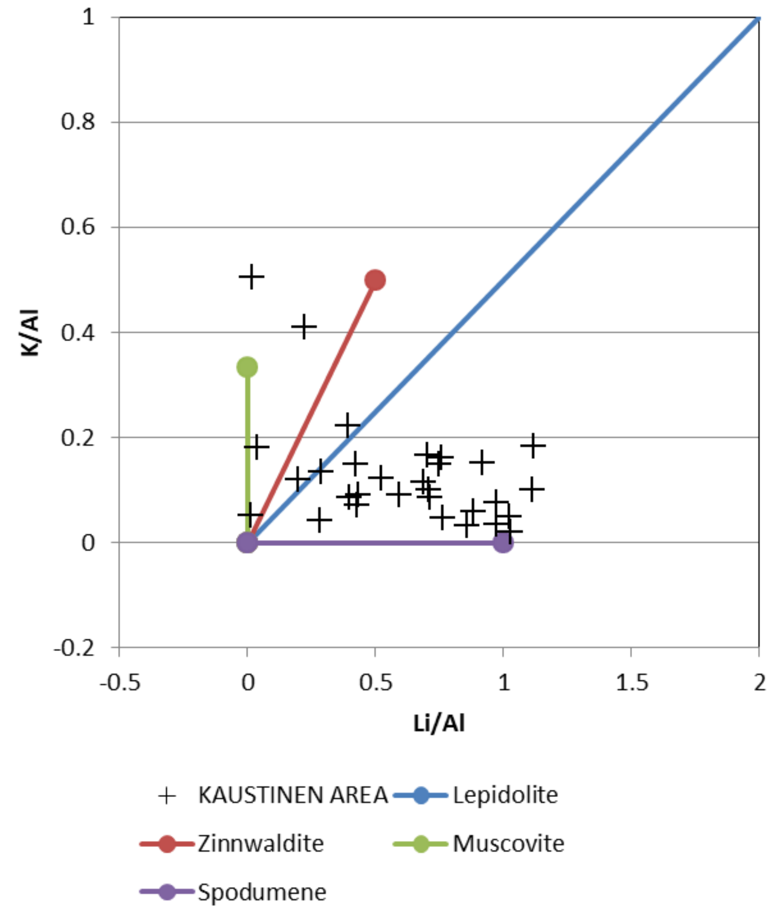
WHAT CAN WR DATA TELL US?

- 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 - SPODUMENE





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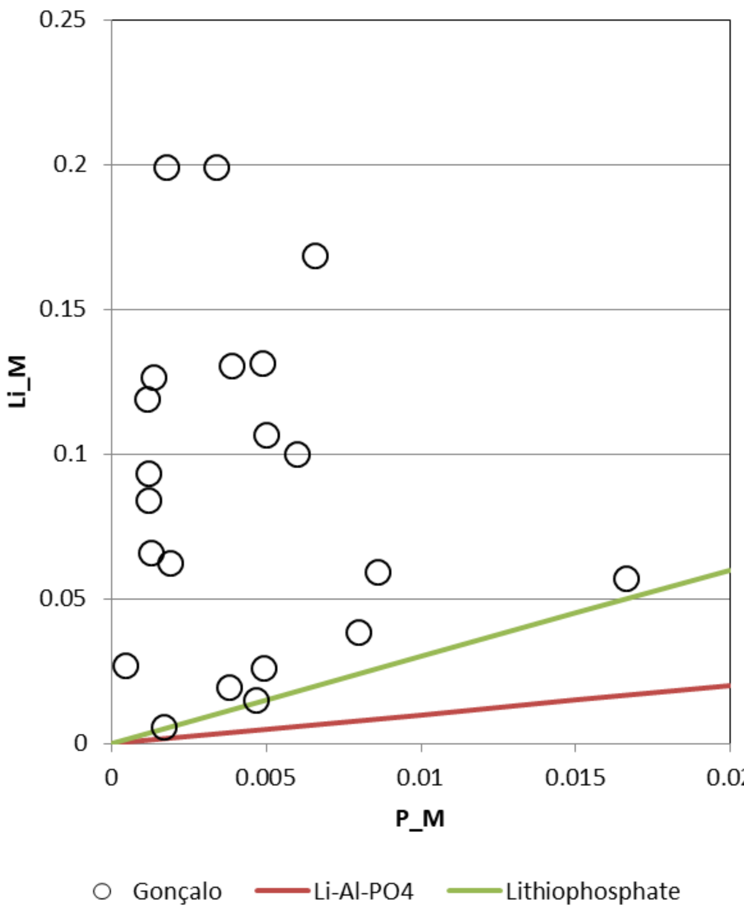
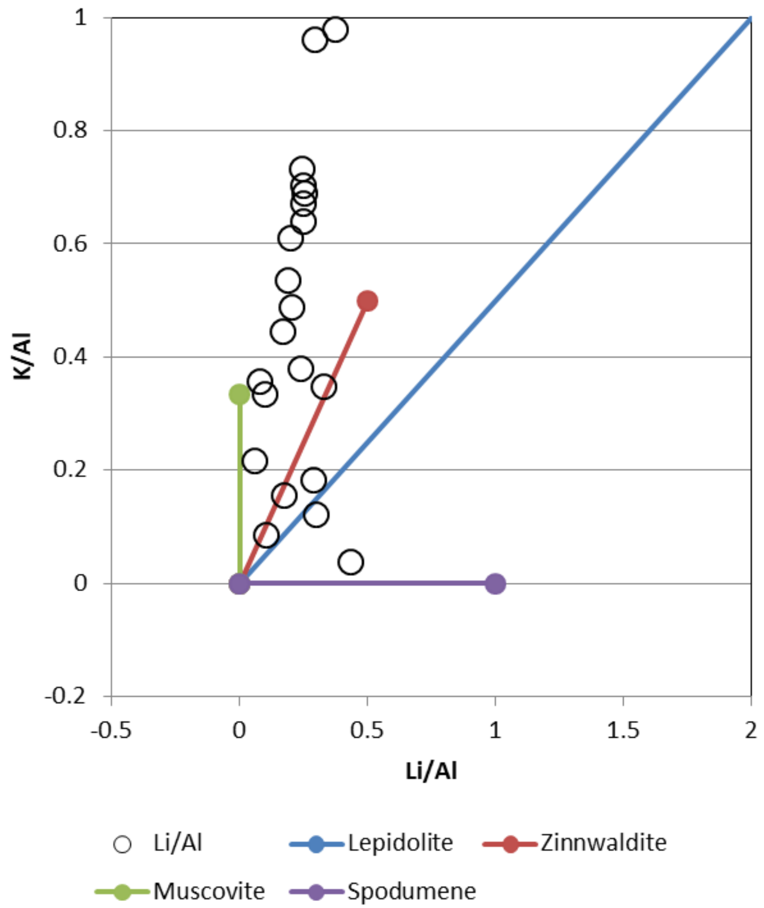
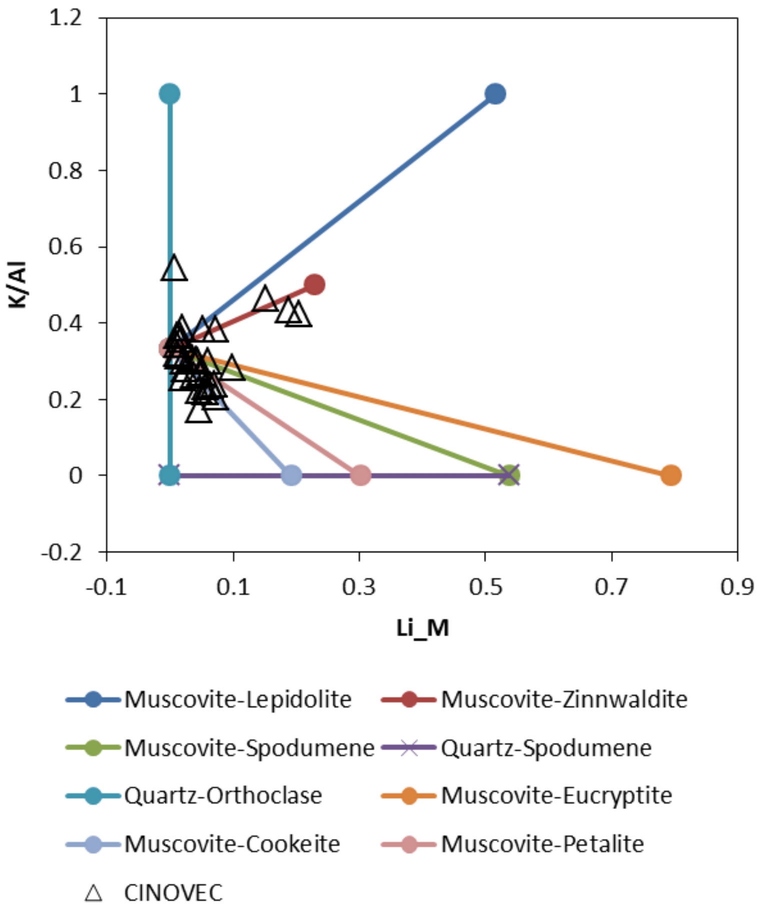
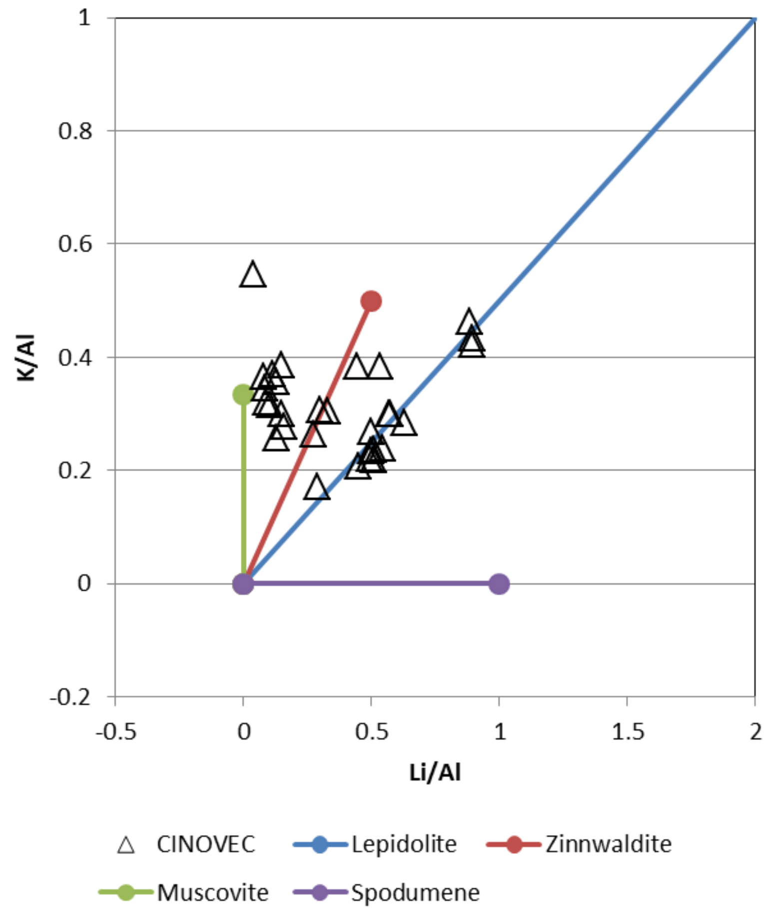
GONÇALO – LEPIDOLITE / Li-PHOSPHATES





CINOVEC – Li-MICAS





WR SUMMARY

- The pre-digestion prep has to be good (fine grind)
- Choose your digestions and finishes careful
- 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 Li±Al±Si±K±Na±Fe±P
- If you want to understand Li deportment in the rock mass you need to do some petrography and mineral chemistry.

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LITHIUM MINERALS (IMA – APPROVED*)

Aleksandrovite	Amblygonite	Balestraite	Balipholite	Baratovite	Berezanskite	Bertossaite	Bikitaite	**Bityite**	Borocookeite
Brannockite	Bulgakite	Clino-ferri-holmquistite	Clino-ferro-ferri-holmquistite	Colquiriite	Cookeite	Cryolithionite	Darapiosite	Dusmatovite	Darrellhenryite
Elbaite	Eliseevite	Emeleusite	Ephesite	**Eucryptite**	Faizievite	Ferri-fluoro-leakeite	Ferri-leakeite	Ferrisicklerite	Ferro-ferri-fluoro-leakeite
Ferro-ferri-pedrizite	Ferro-holmquistite	Ferro-pedrizite	Fluor-elbaite	Fluor-liddicoatite	Fluoro-leakeite	Gainesite	Garmite	Gorbunovite	Griceite
Griphite	**Hectorite**	Holmquistite	Hsianghualite	**Jadarite**	Katayamalite	Lavinskyite	Liberite	Lintisite	Lithiomarsturite
Lithiophilite	Lithiophorite	**Lithiophosphate**	Lithiotantite	Lithiowodginite	Luanshiweiite	Lunijianlaite	Magnesioneptunite	Magnesiostaurolite	Manandonite
Mangani-dellaventuraite	Manganoneptunite	Masutomilite	Mccrillisite	**Montebrasite**	Murakamiite	Nalipoite	Nalivkinite	Nambulite	Nanlingite
Natronambulite	Neptunite	Norrishite	Olympite	Orlovite	Oxo-mangani-leakeite	Pahasapaite	Palermoite	Peatite-(Y)	**Petalite**
Pezzottaite	Piergorite-(Ce)	Polylithionite	Potassiccarpholite	Potassic-ferri-leakeite	Potassic-mangani-leakeite	Punkaruaivite	Ramikite-(Y)	Rossmanite	Saliotite
Sicklerite	Silinaite	Simferite	Simmonsite	Sogdianite	Sokolovaite	**Spodumene**	Sugilite	Swinefordite	Tainiolite
Tancoite	Tanohataite	Tavorite	Tiptopite	Trilithionite	Triphylite	Virgilite	Voloshinite	Walkerite	Watatsumiite
	Wilancookite	Zabuyelite	Zektzerite	***Lepidolite***	*Zinnwaldite*	*Li-muscovite*	*Li-phengite*		

MINERALS EXAMINED

Name	Formula	Li (wt%)	Dana Class	Hardness
Spodumene	$LiAlSi_2O_6$	3.73	Inosilicate (Pyroxene)	6.5-7
Eucryptite	$LiAlSiO_4$	5.51	Nesosilicate (Phenakite group)	6.5
Petalite	$LiAl(Si_4O_{10})$	2.09	Phyllosilicate	6.5
Montebrasite	$LiAl(PO_4)(OH)$	4.74	Anhydrous Phosphates (Amblygonite Group)	5.5-6
Lithiophosphate	Li_3PO_4	17.98	Anhydrous Phosphates (Lithiophosphate Group)	4
Hectorite	$Na_{0.3}(Mg,Li)_3(Si_4O_{10})(F,OH)_2$	0.54	Phyllosilicate (Smectite group)	1-2
Lepidolite	$KLi_2Al(Si_4O_{10})(F,OH)_2$ to $K(Li_{1.5}Al_{1.5})(AlSi_3O_{10})(F,OH)_2$	3.58	Phyllosilicate (Mica group)	2.5-3.5
Jadarite	$LiNaSiB_3O_7OH$	3.38	Nesosilicate (Howlite and related species)	4 - 5
Bityite	$CaLiAl_2(AlBeSi_2)O_{10}(OH)_2$	1.79	Phyllosilicate (Mica group)	5.5

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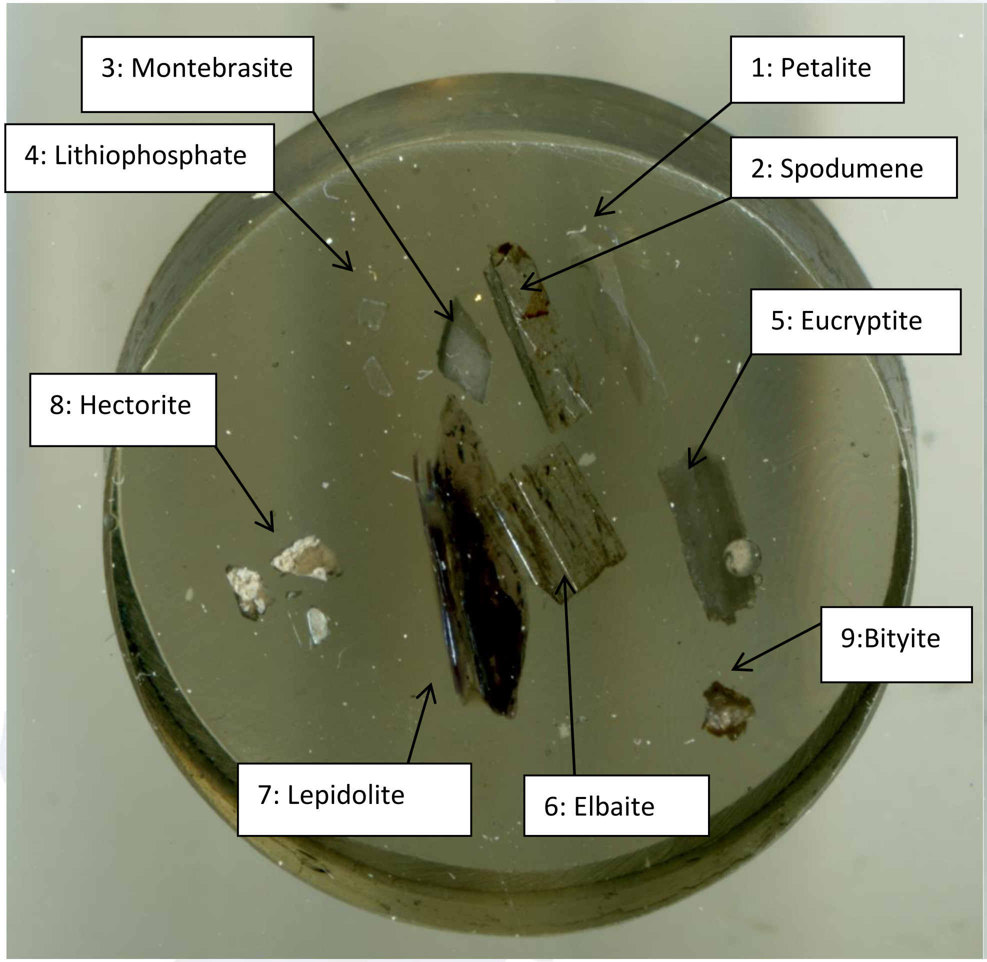
BLOCK IMAGES



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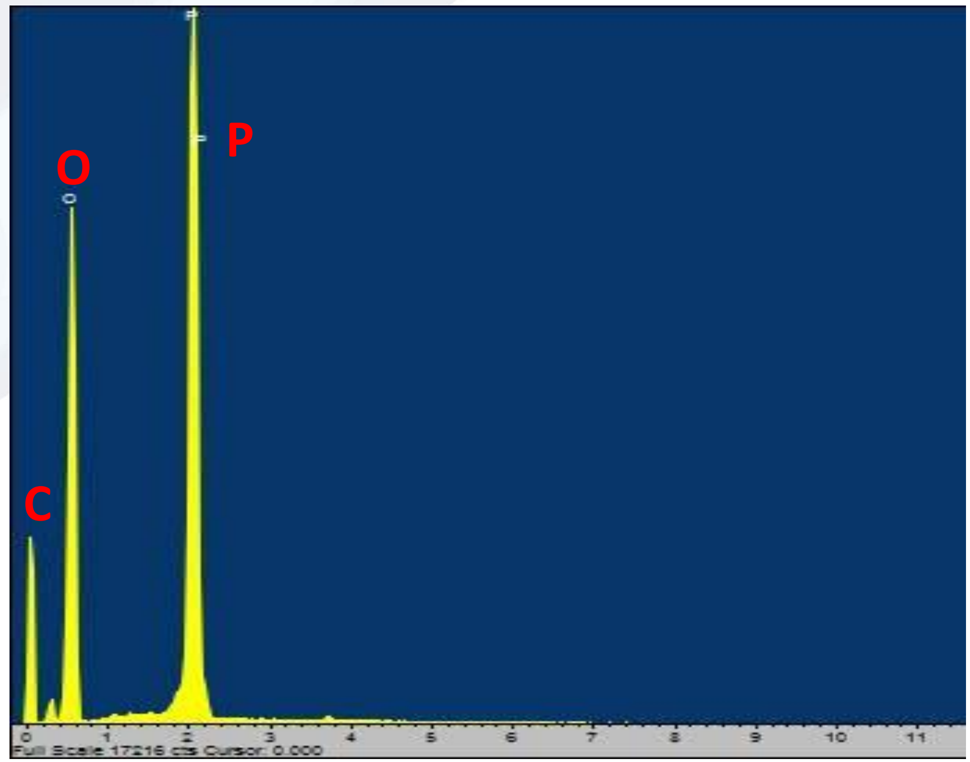
ELECTRON BEAM TECHNIQUES AND Li-MINERALS

- 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)

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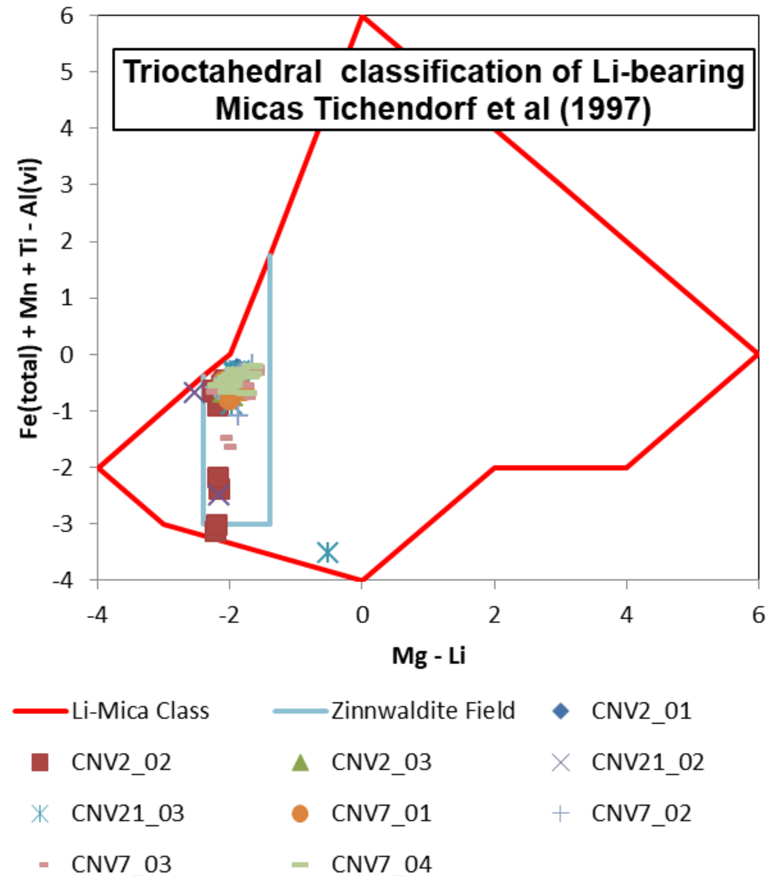
THERE DO EXISTS PROTOCOLS FOR PARTICULAR MINERALS USING EPMA

- For example:
- Tischendorf, Forster & Gottesmann (1999) for estimation of Li in trioctahedral micas (Mg)
- Tindle & Webb (1990) estimation of Li in trioctahedral micas (Si)

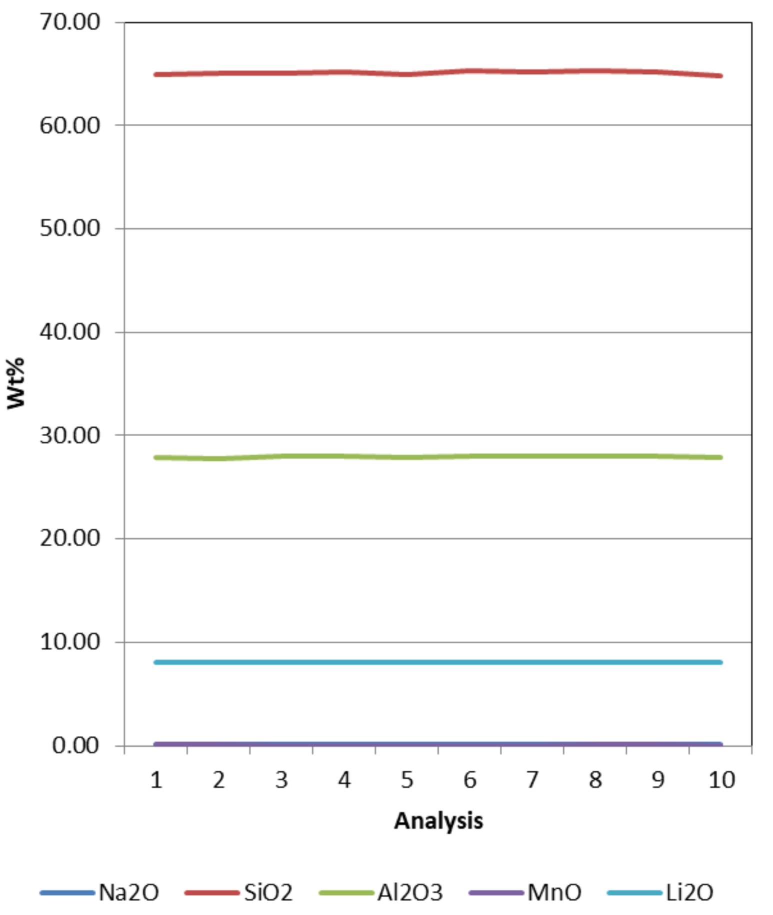


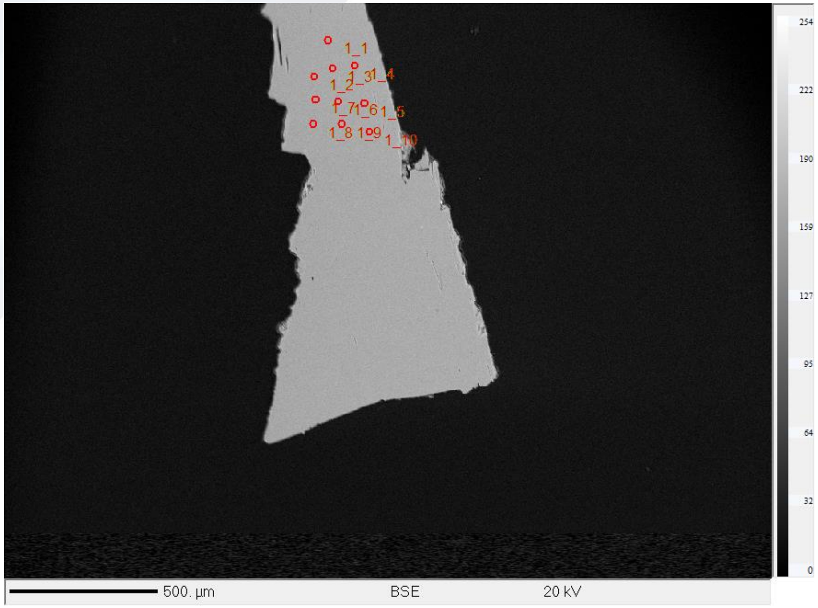
EPMA – ANALYTICAL CONDITIONS

Sp	Elements	X-ray line	Xtal	Time (S)	DLS (ppm)
Sp2	F	Kα	LPC0	30	759
Sp4	Na	Kα	TAP	10	289
Sp4	Si	Kα	TAP	20	239
Sp4	Mg	Kα	TAP	20	147
Sp4	Al	Kα	TAP	20	191
Sp4	P	Kα	TAP	20	261
Sp1	Cl	Kα	PET	10	426
Sp3	K	Kα	LPET	10	209
Sp1	Ca	Kα	PET	30	169
Sp5	Mn	Kα	LLIF	20	248
Sp5	Fe	Kα	LLIF	20	243
Sp5	Rb	Kα	LLIF	30	3760
Sp3	Ti	Kα	LPET	20	148
Sp3	Sr	Lα	LPET	30	606
Sp3	Cs	Lα	LPET	30	436
Sp1	Ba	Lα	PET	20	776

- CAMECA SX100
- Natural History Museum
- Beam current 20nA
- Accelerating voltage 20kV
- Spot size 3µm

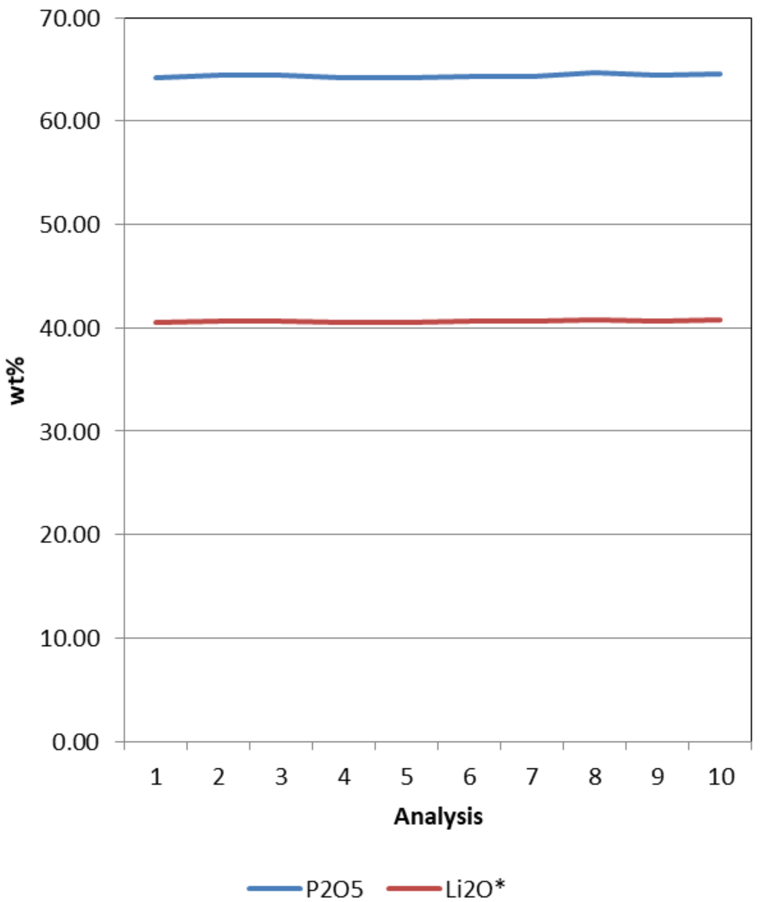
SPODUMENE

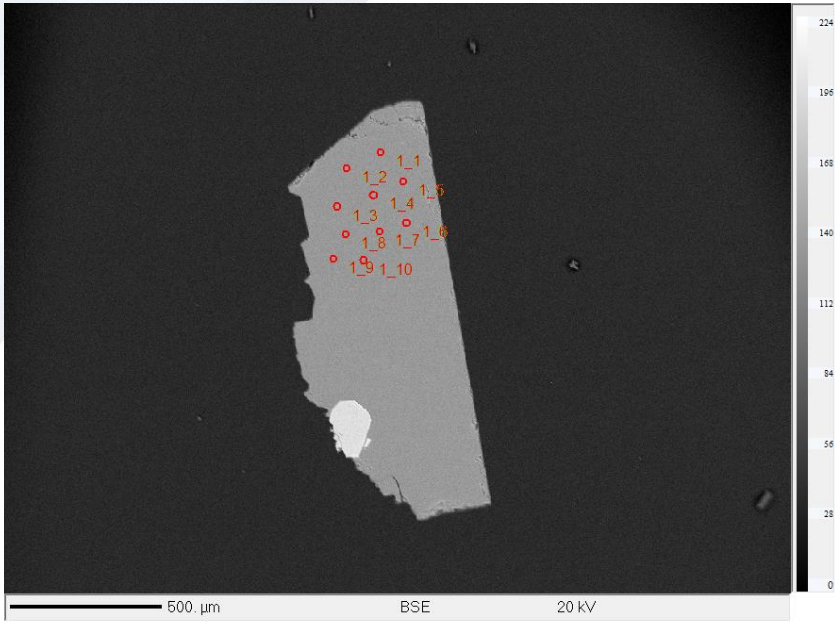




- Average Li (wt%) = 3.74
- Literature Li (wt%) = 3.73

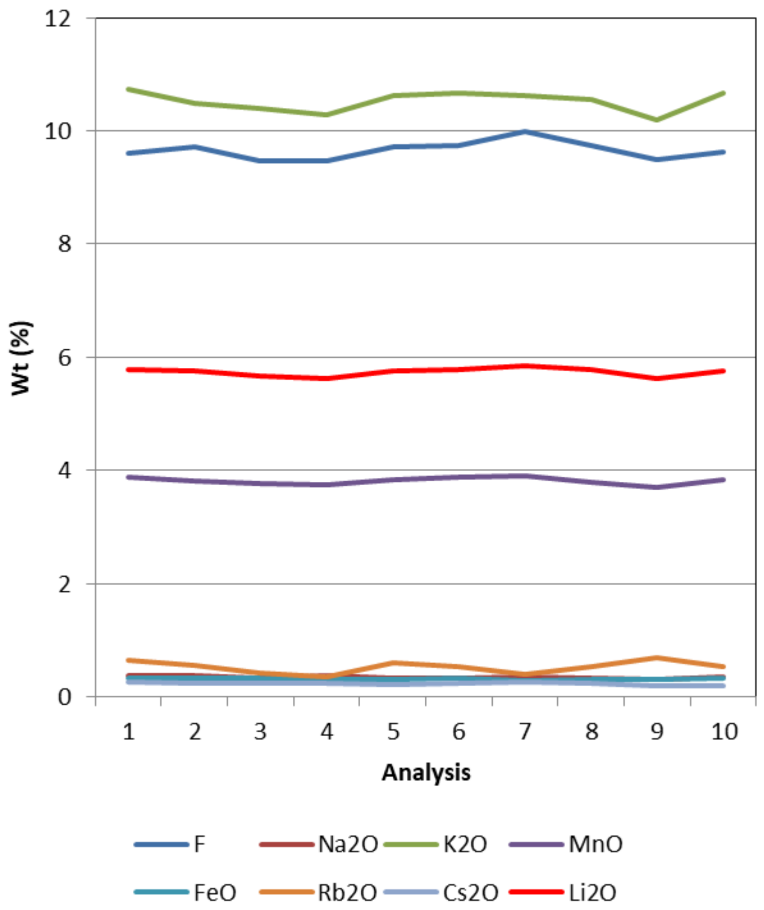
LITHIOPHOSPHATE

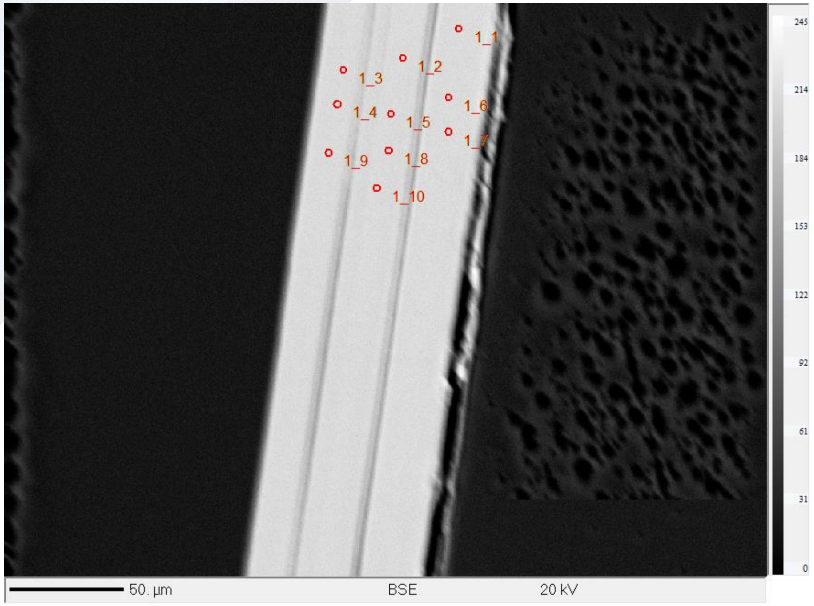




- Average Li (wt%) = 18.88
- Literature Li (wt%) = 17.98

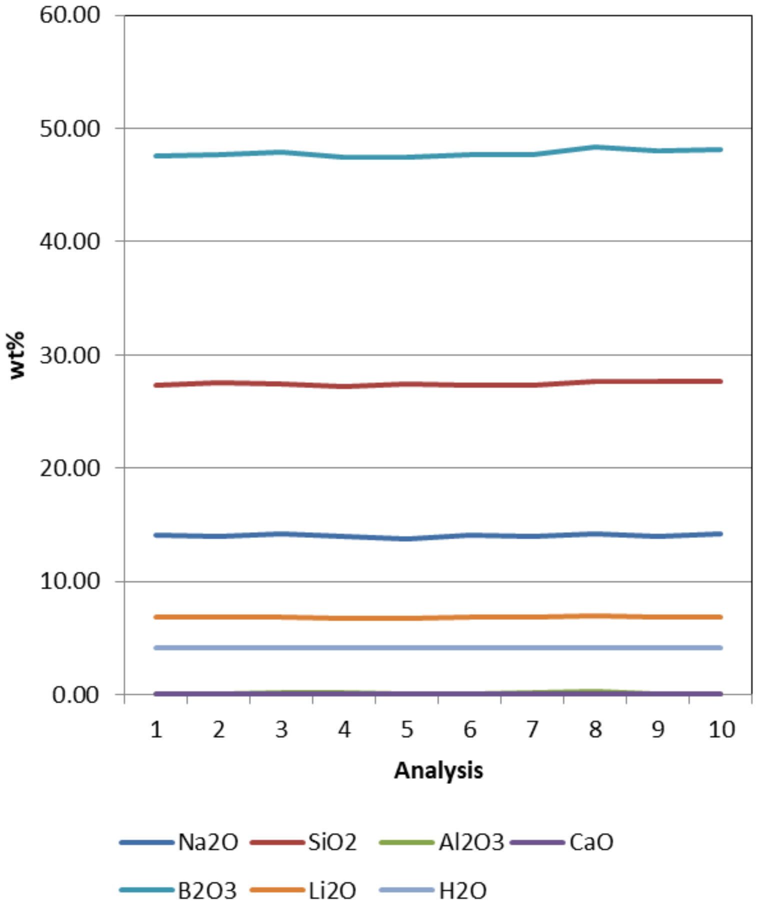
LEPIDOLITE

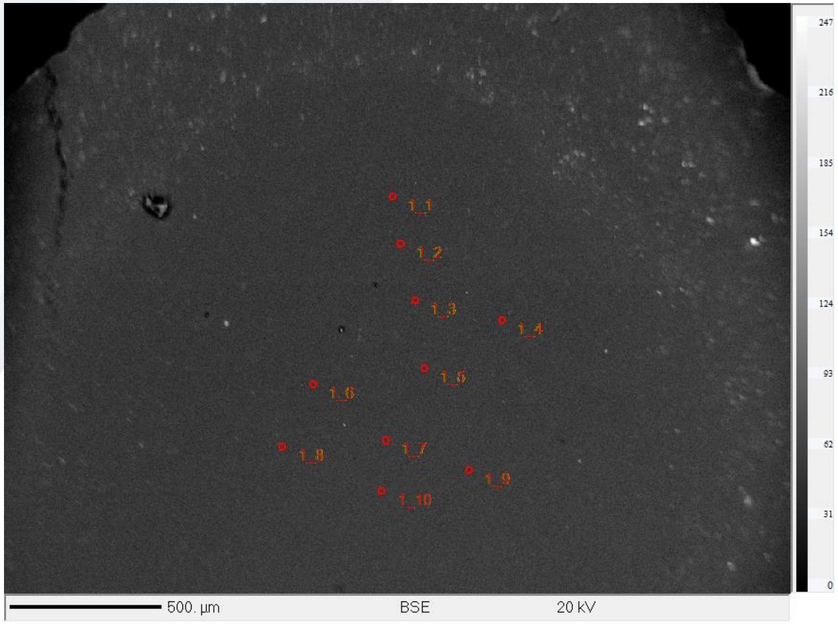




- Average Li (wt%) = 2.67
- Literature Li (wt%) = 3.73

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

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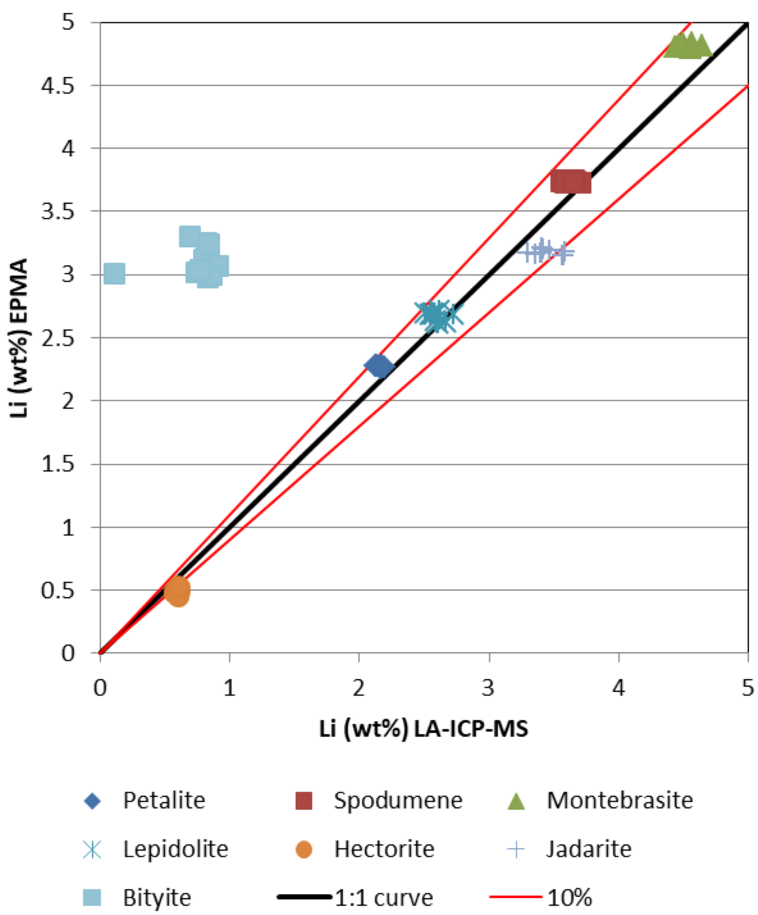
COMPARING Li VALUES: LA-ICP-MS VS EPMA



- 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

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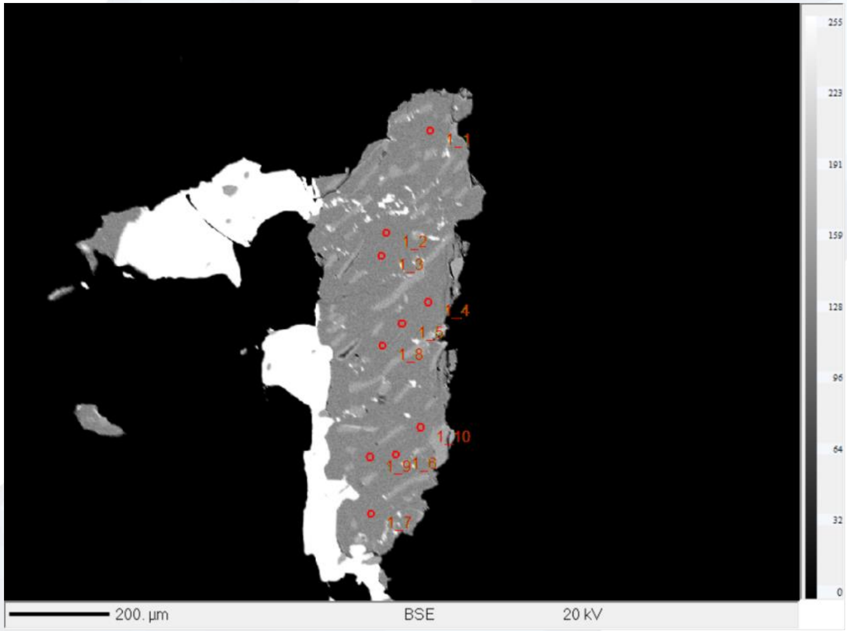
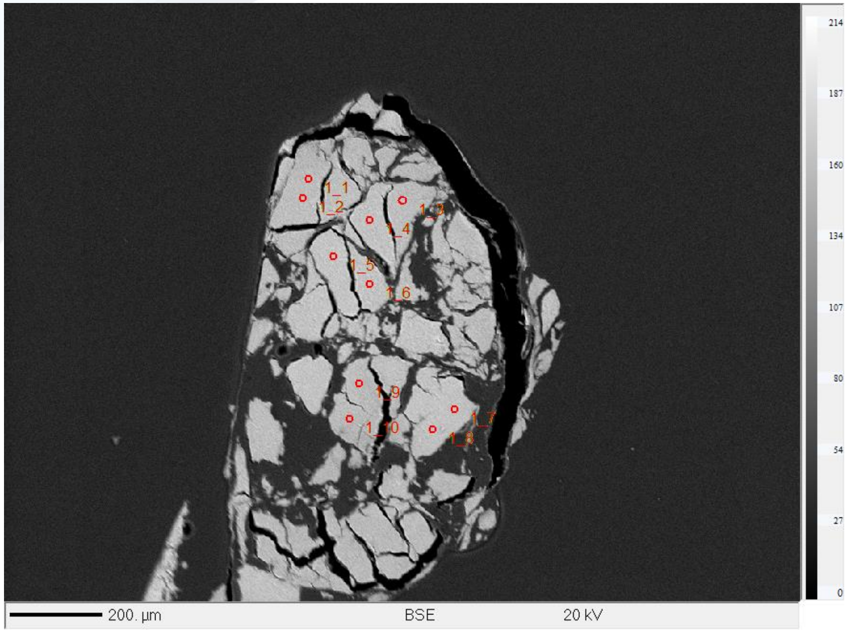
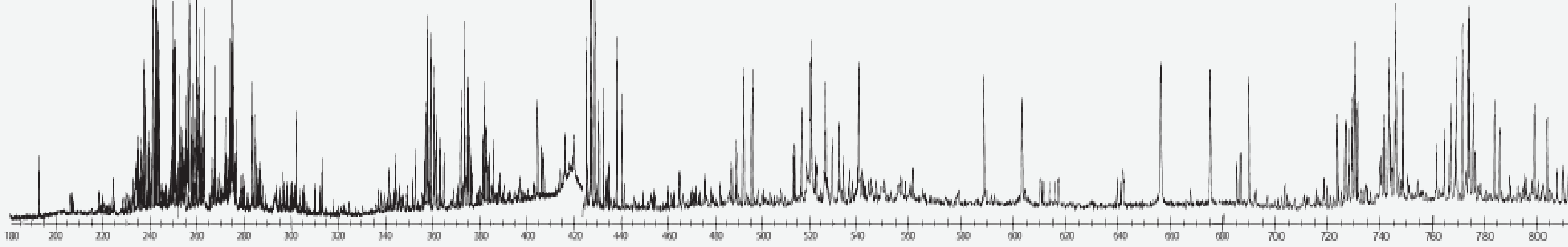
LA-ICP-MS VS EPMA CONTINUED

- Bityite



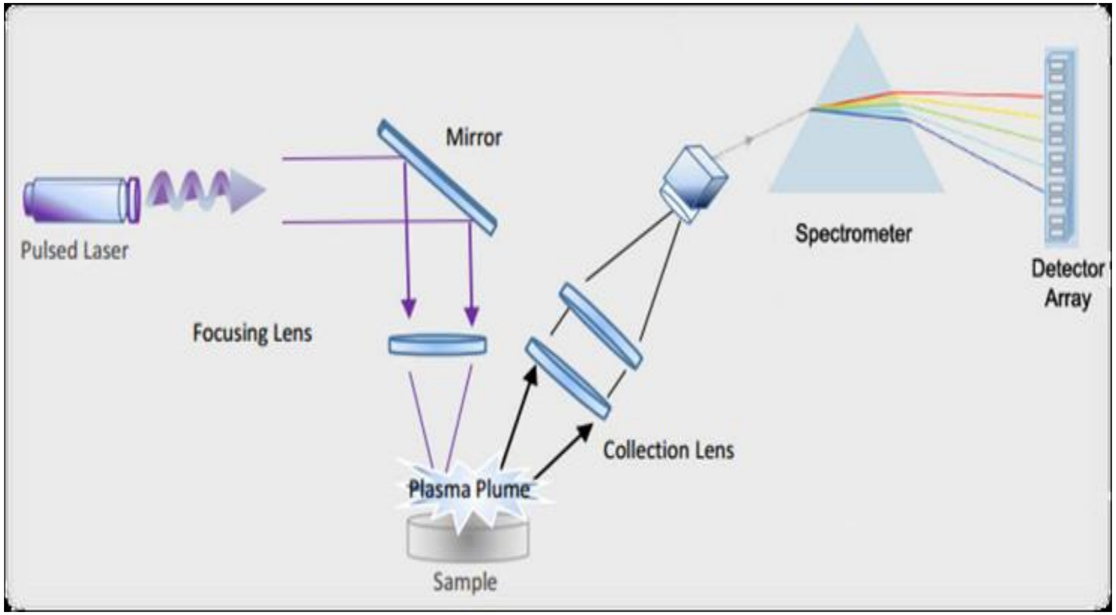
- Hectorite



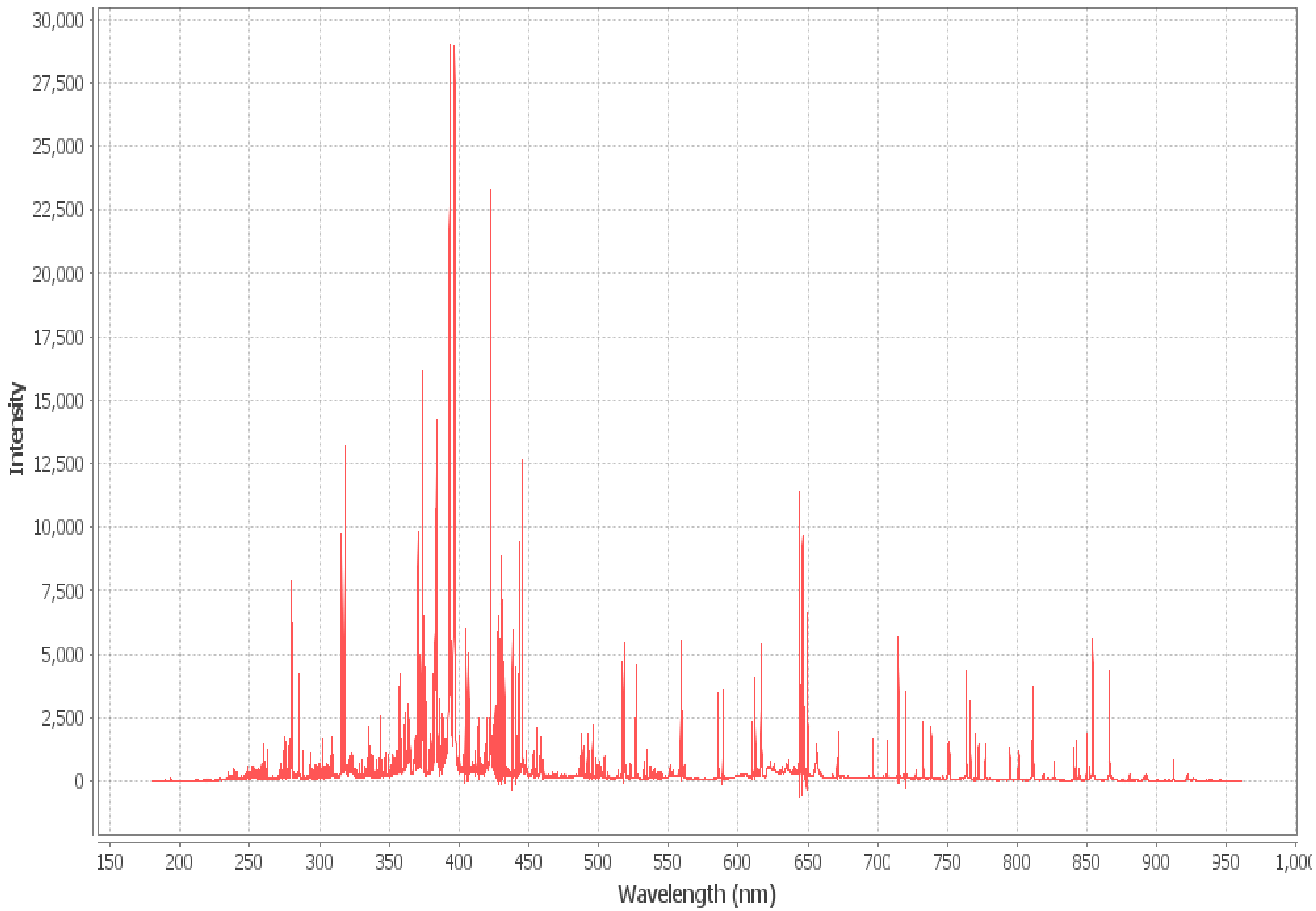


LIBS (Laser Induced Breakdown Spectroscopy)

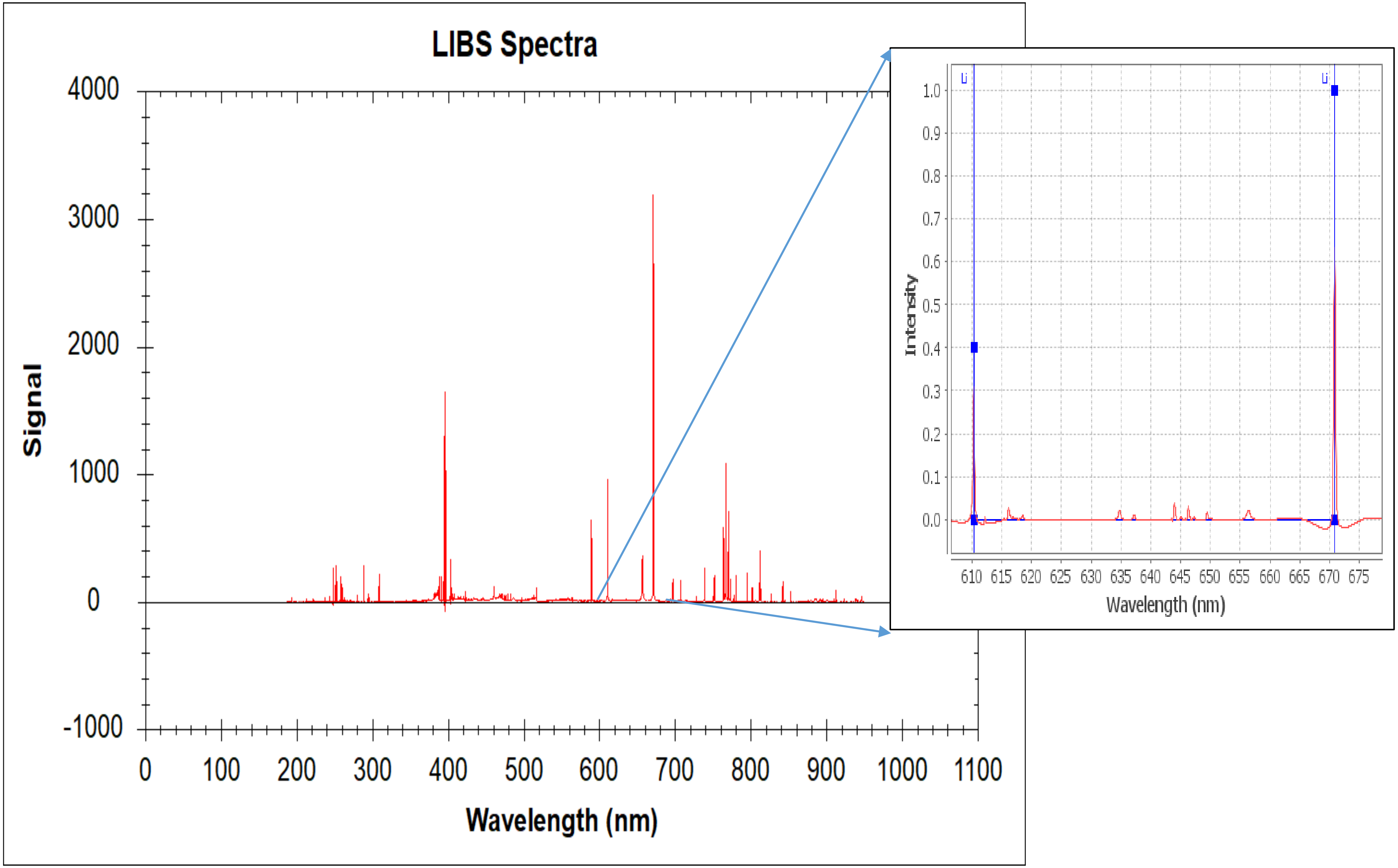
- Optical Atomic Emission Spectroscopy (OES)
- Focused laser ablates surface to create a plasma
- Light from plasma is collected, run through a spectrometer and projected onto the detector creating a spectrum (x – wavelength, y – intensity)



SciAps Z300 Hand Held LIBS Spectra: 190-950nm

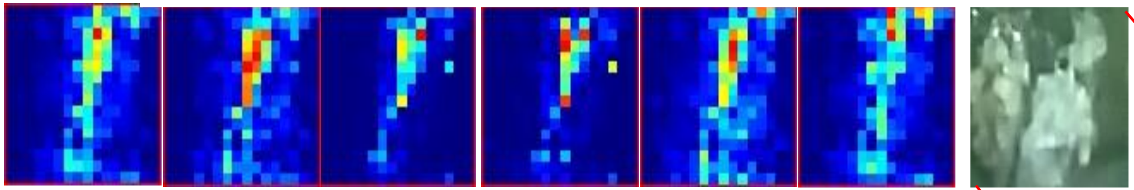


Li peaks used for direct measurement



Lepidolite

$KLi_2Al(Si_4O_{10})(F,OH)_2$ to $K(Li_{1.5}Al_{1.5})(AlSi_3O_{10})(F,OH)_2$



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

Comparison of results using different analytical techniques

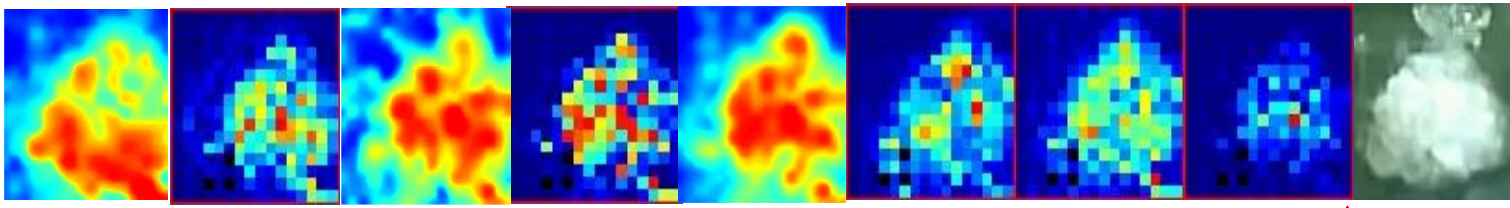
	Li	Be	Al	Si	Na	K
LIBS	3.1602	0.0003	10.898	11.5469	0.5623	18.2149
LA ICP MS	2.5968	0.002682	Not analysed	21.497	0.18733	8.5802
EPMA	1.4496*	Not analysed	12.2313	22.5672	0.2557	8.7195

*Rb by LA ICP-MS=0.8227%

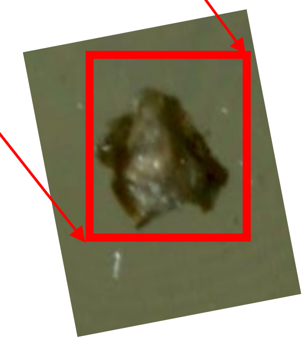
* Not analysed but calculated by difference

Bityite

$CaLiAl_2(AlBeSi_2)O_{10}(OH)_2$



Ca 445.478nm Li 670.79nm Be 313.041nm Al 396.152nm Si 288.158nm K 766.49nm



Comparison of results using different analytical techniques

	Li	Be	Al	Si	Na	K	Ca
LIBS	1.4496	0.0002	10.4426	-42.6703	-0.0403	4.488	0.3062
LA ICP MS	0.7366	0.001122	Not analysed	10.471	0.030534	0.95056	0.0412
EPMA	**3.1014***	Not analysed	14.6695	30.3558	0.0912	0.0035	-0.0015

* Not analysed but calculated by difference

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.

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GTK NATURAL HISTORY MUSEUM EUROPEAN metals GEOKOMPETENZ wardell armstrong LNEG LULEÅ TEKNISKA UNIVERSITET G.E.O.S. INGENIEUR-GESELLSCHAFT MBH U.PORTO UNIVERSITY OF EXETER UNIVERSITÉ DE LORRAINE GBM brgm COLT resources KELIBER