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APPLICATION NOTE

Compositional and traceability analysis of lithium ores and concentrates by LA-ICP-MS and GDMS

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INTRODUCTION

Lithium-ion batteries (LIBs) are an essential technology for the clean energy transition currently in progress across the globe. LIBs power everything from smart phones and implantable medical devices to electric vehicles (EVs) and whole home backup power systems. The market for LIBs will only increase as the need for advanced energy storage grows hand-in-hand with the broad adoption of renewable energy sources like wind turbines and solar panels. A recent study by McKinsey Battery Insights[1] found that the LIB supply chain is expected to grow by ~30% annually through 2030, by which time the global demand for LIB capacity is estimated to reach ~4700 Gigawatt hours (GWh) from ~700 GWh in 2022. Demand will overwhelmingly be driven by mobility applications like EVs, with stationary storage and consumer electronics demand also anticipated to grow simultaneously. The tremendous economic opportunity represented by LIBs as part of the clean energy transition is accompanied by the responsibility to overcome the environmental, social, and governance challenges that the battery value chain will face from mining through recycling. As a leading global scientific services provider with deep experience in materials science and engineering disciplines, Eurofins EAG Laboratories stands ready to help clients working in all stages of the battery value chain achieve their business goals and contribute to the decarbonization of the global economy.

Lithium ore, also known as hard-rock lithium, is derived from mining and is one of the two major raw material sources for lithium production for industrial applications. The other source is continental lithium brines in which lithium weathers out of rock, is transported in solution by water, and then is trapped in inland basins and naturally concentrated by evaporation. This application note will focus on hard rock lithium. The most important minerals for lithium mining are spodumene (Li_2O, $Al_2O_3{\cdot}4SiO_2$) and petalite (Li_2O, $Al_2O_3{\cdot}8SiO_2$). Both minerals occur in granitic pegmatites, a type of igneous rock characterized by its coarse texture and mineralogical composition dominated by quartz, feldspar, and mica.

Greenbushes, located in Western Australia, is the spodumene mine from which lithium ore reference materials studied in this application note were sourced.

Many of the minerals in pegmatites are resistant to the acid digestion procedures used to prepare rock samples for elemental analysis by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). As an alternative to aqua regia (HNO_3 and HCl) or four-acid digestion (HNO_3, HCl, H_2SO_4, and $HClO_4$), service laboratories for the extractive industries largely rely on sodium peroxide fusion followed by acidification with hydrochloric and nitric acids for complete decomposition of hard rock lithium ores for solution analysis. However, fusion approaches come with their own disadvantages. The high temperatures involved in fusion can lead to volatilization and loss of certain elements. Fusion can introduce unintended impurities from the sodium peroxide flux affecting the accuracy and reliability of the elemental analysis; furthermore, the addition of sodium from the flux will always render that element unquantifiable. Another issue is the incomplete decomposition of certain minerals in the rock matrix. Some refractory minerals may resist decomposition even in a fusion preparation, resulting in incomplete extraction of elements of interest. This can lead to underestimation of certain elements in the sample. Finally, the presence of fusion and digestion reagents in the digested sample can cause interferences on certain analytes measured by ICP-OES and ICP-MS that may be challenging or impossible to mitigate. While peroxide fusion is a robust sample preparation technique, its limitations make elemental analysis of hard rock lithium an application ripe for disruption by a new approach.

Compositional and traceability analysis of lithium ores and concentrates by LA-ICP-MS and GDMS

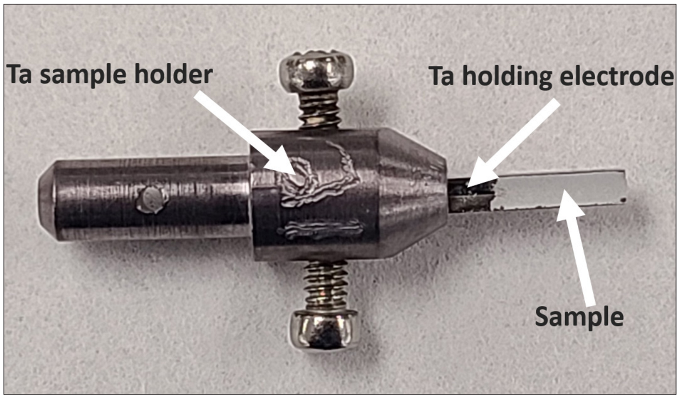

Figure 1: Lithium ore reference material on a Ta holding electrode.

Solid-state analysis of rock samples can overcome many of the aforementioned limitations, while simultaneously reducing turnaround time and generation of hazardous waste by eliminating the sample digestion steps. X-Ray Fluorescence (XRF) is a widely available solid-state elemental analysis technique that can be field-portable and non-destructive in some applications. However, it cannot routinely detect elements below atomic number twelve (magnesium), whereas lithium has an atomic number of three. As a result, the best XRF can do for lithium ore is to measure elements associated with lithium-bearing pegmatite mineralization and predict lithium content indirectly. While this can be a useful and cost-effective approach to geochemistry during the exploration phase of the mineral discovery lifecycle[2], it is insufficient for assaying ore from an operating mine or for lithium concentrates produced further down the supply chain.

The Eurofins EAG Laboratories Purity Survey business line has a long record of expertise in two techniques uniquely suited to the challenge of solid-state elemental analysis of lithium ores: Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and Glow Discharge Mass Spectrometry (GDMS). LA-ICP-MS was invented for geochemical applications and is reliant upon calibration with matrix-matched reference materials and sample-standard bracketing to yield quantitative concentration results. In contrast, GDMS was initially developed for analysis of high purity conductive materials like metals and alloys without the need for external calibration of each experiment because of the use of generalized calibration factors. Decades of work by the Purity Survey business line of EAG Laboratories has led to the development of procedures for reliable GDMS analysis of semi-conductive, non-conductive, and refractory compounds like silicon carbide, boron carbide, aluminum oxide, and other ceramic materials. Co-sputtering a non-conductive sample with a conductive tantalum (Ta) holding electrode in pin cell configuration (Figure 1), coupled with the recent experimental development of Relative Sensitivity Factors (RSFs) specifically for mixed oxides[3], has extended the reach of trace elemental analysis by GDMS to raw materials for the LIB supply chain.

EXPERIMENTAL DESIGN

In this study, we sought to test the viability of "full scan" (~69 elements) compositional analyses of lithium pegmatite ore as solid samples using a combination of LA-ICP-MS and GDMS. The premise was that empirically calibrated LA-ICP-MS using matrix-matched reference materials provides fully quantitative concentrations for elements expected to routinely occur in the weight percent through hundreds of parts per million (ppm) range in hard rock lithium. Specifically, LA-ICP-MS was responsible for measuring Li, Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe. GDMS was responsible for measuring all other non-gas forming elements which are expected to occur in the range of hundreds of ppm and lower. The intended use case for the resulting data has two facets: 1) The LA-ICP-MS dataset comprises the elements of interest for initial ore characterization and spodumene concentrate characterization through the beneficiation process. 2) The GDMS dataset provides complementary information about minor through trace elements that may be a) economically exploitable or b) useful for supply chain integrity/ore traceability (*i.e.*, provenience) applications.

To test the viability of these two techniques, we acquired a series of commercially available lithium pegmatite ore reference materials (RMs) for analysis. The five RMs were manufactured by OREAS Pty. Ltd. (Australia) from lithium pegmatite mine tailings and range from unprocessed ore to spodumene concentrate. The RMs are sold as bulk powders and are not intended for LA-ICP-MS due to the coarseness of the particles and wide particle size distribution. EAG partnered with myStandards GmbH of Kiel, Germany, a leading manufacturer of nanopowder RMs for microanalytical applications. myStandards provided nanopowder versions of all five OREAS reference materials, both as loose nanopowders and as binder-free nanopowder pressed pellets.

METHODS

Nano-Pellet Production

The nanopowder pressed pellets, so-called Nano-Pellets (Figure 2, next page), used in this application were made from commercially available certified reference materials from OREAS, namely, the Li ore series 750–753 plus

OREAS 999 (spodumene concentrate). By implementing the wet-milling protocol at myStandards GmbH, the particle size was reduced from the µm-range to the nm-range, with a d^{90} of approximately 300 nm. This improved both compressibility of the nanopowder and cohesion of the resulting Nano-Pellet.

The wet milling was performed in a high-power planetary ball mill using agate (SiO_2) milling beakers, balls and deionized water. After milling the resulting slurry was pipetted into borosilicate flasks and frozen in a conventional freezer. Once the slurry was completely frozen the flasks were attached to a freeze-dryer. Freeze-drying, despite being more time-consuming, is preferable to oven drying as the resulting powder is more manageable. Further, temperatures of 60–100° C in an oven may already cause low-grade metamorphic reactions and the finished sample needs to be broken apart in a pestle and mortar again increasing risk of sample loss and contamination.

The dried samples were placed in a mixer mill for homogenization. This step is necessary, as rocks consist of a large variety of minerals with varying densities. Denser minerals will settle more quickly while the slurry is stationary in the flask, whereas less dense minerals will settle more slowly, causing a stratification and heterogenous distribution. The homogenized nano-powder was weighed out and pressed to Nano-Pellets in an automated programmable hydraulic press ensuring a reproducible process.

LA-ICP-MS Analysis

OREAS 750–753 were analyzed as quality control reference materials for method validation, with OREAS 999 (spodumene concentrate) used as the single point external calibrant with sample-standard bracketing. Internal standardization was carried out using the measured ^{29}Si signal and the certificate reference value for total silicon content. All data reduction was carried out in Iolite v4 (Elemental Scientific Lasers) using the Trace Elements data reduction scheme.

OREAS Nano-Pellets 750–753 were ablated with five replicate scan lines per day on five different days (n = 25) using the same laser parameters each time (Figure 2). This approach allowed us to account for instrumental drift over the course of multiple days of analysis when calculating reproducibility of concentrations. All LA-ICP-MS analyses were carried out with an ESL imageGEO 193 laser ablation system coupled to a Thermo Scientific iCAP TQ (ICP-MS/MS). Basic instrument parameters are provided in Table 1.

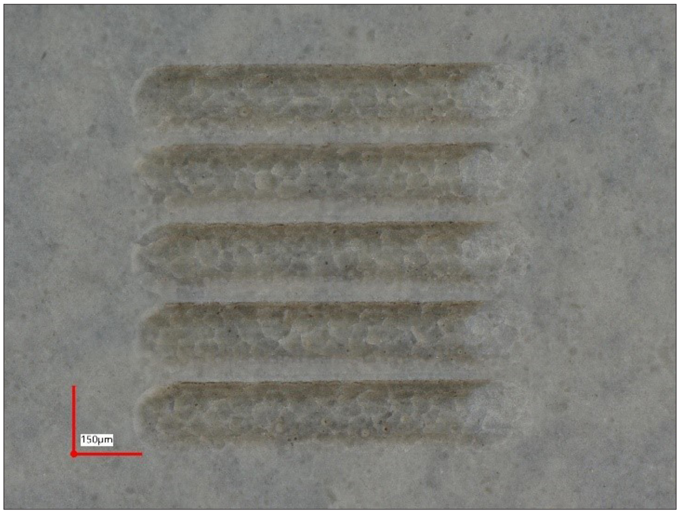

Figure 2: Five ablation scan line troughs on the OREAS 999 Nano-Pellet.

GDMS Analysis

GDMS analysis was performed using multiple Ametek Nu Instruments Astrum ES glow discharge mass spectrometers. Approximately 10 mg of nanopowder per sample analysis were packed onto a Ta sample holding electrode. Electrodes were pre-cleaned with a hydrofluoric and nitric acid solution to mitigate possible sample cross-contamination. The samples were analyzed using glow conditions of 3.0 mA fixed current and a voltage of 1.0 kV, with the argon flow adjusted to achieve the desired voltage. Specific isotopes were selected based on matrix composition to avoid or mitigate the impact of isobaric interferences.

ICP-MS Parameters (Thermo Scientific iCAP TQ)
ICP-MS Mode: Single Quadrupole – Kinetic Energy Discrimination
Plasma Power: 1300 W
Dwell time per isotope: 0.1 sec
Laser Parameters (ESL imageGEO 193)
Laser Spot Size: 150 µm
Scan Line Length: ~1 mm
Scan Speed: 5 µm/sec
Repetition Rate: 20 Hz
Fluence: 1.5 J/cm^2
Carrier Gas: 0.85 L/min He

Table 1: Instrumentation parameters for LA-ICP-MS.

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LA-ICP-MS Results

The Nano-Pellet lithium ore and concentrate reference materials exhibited favorable ablation behavior, having acted more like a cohesive solid (*e.g.*, a glass microanalytical reference material) than a typical pressed pellet made of non-nanopowder loose material. There was no gross visual evidence of redeposition of ablated material or of undesirable thermal effects like cracking, melting, or charring either within or adjacent to the ablation patterns (Figure 2, previous page). Post-ablation 3-dimensional composite microscopy using a Keyence VHX digital optical microscope was used to assess the depth of scan line troughs. Figure 3 shows a typical example from the OREAS 999 Nano-Pellet. Troughs were at their deepest 45–50 µm below the pellet surface. The gradation in depth from the edge of each scan line to its center (red to green to blue symbology) illustrates that the troughs lack the ideal cylindrical cross-section and are more V-shaped.

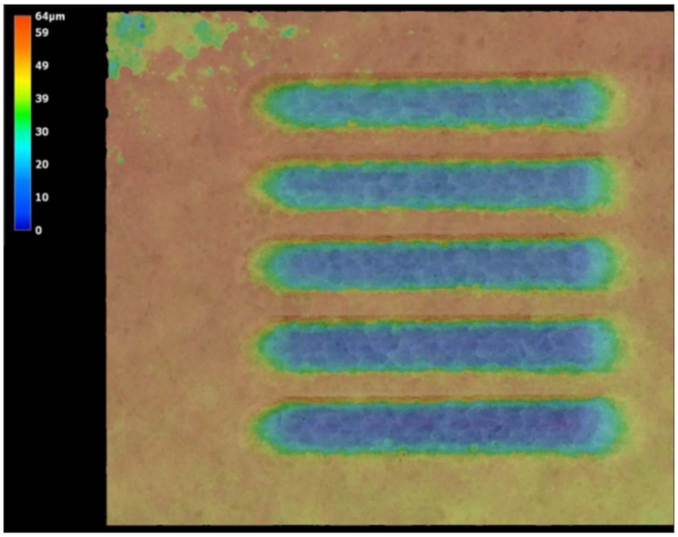

Figure 3: False color depth composite heat map of five ablation scan line troughs on the OREAS 999 Nano-Pellet.

For OREAS 750–752, all analytes exhibited overall mean recovery within 10% of reference values. OREAS 753 showed recovery within 25% of reference values for Mg, Ca, and Ti and within 10% for the other elements. Mean recovery ratios were calculated relative to the certificate values in Table 2 and are reported in Table 3. RSD% were generally quite low; out of eleven elements measured in five samples (55 calculations of RSD%) only two exceeded 10% RSD: 18% for P in OREAS 753 and 11% for Ca in OREAS 753 (Table 3).

GDMS Results

Table 4 on pages 6–7 shows the mean percent recovery and the inter-sample variance of the OREAS suite of reference materials. Of the 54 analyzed elements, including elements with indicative values on their certificates, 10 were within 10% recovery, 19 were within 25% recovery, and 47 were within a factor of two of the certificates – the expected methodological precision range for the GDMS method used. More importantly, the inter-sample variance of the measured elements across all five OREAS powders was generally better than 25%, with 45 of the 54 elements exhibiting less than 25% inter-sample variability.

DISCUSSION AND CONCLUSIONS

The premise of the LA-ICP-MS portion of this study is that laser ablation can provide fully quantitative major and minor element compositional analysis of hard rock lithium ores and ore concentrates without the need for time consuming acid digestion, or fusion followed by digestion, that requires multiple hazardous reagents and can lead to the loss of volatile elements. This study measured four spodumene ore reference materials as nanopowder pressed pellets and assessed the viability of using LA-ICP-MS as described above, with success/failure determined by the metrics % recovery and relative standard deviation % for 11 elements of interest. Generally, recovery and RSD were excellent as described in the Results.

Source	RM #	Li wt. %	Na wt. %	Mg wt. %	Al wt. %	Si wt. %	P wt. %	K wt. %	Ca wt. %	Ti wt. %	Mn wt. %	Fe wt. %
OREAS	999	2.65	0.693	0.410	12.23	30.30	0.016	0.500	0.450	0.034	0.143	1.62
OREAS	753	0.985	2.16	0.011	8.22	34.45	0.111	1.93	0.113	0.004	0.074	0.839
OREAS	752	0.695	2.7	0.044	7.94	34.18	0.140	2.08	0.199	0.016	0.079	0.835
OREAS	751	0.463	2.47	0.287	8.01	33.23	0.124	2.41	0.742	0.144	0.065	1.62
OREAS	750	0.232	1.53	0.315	5.42	36.87	0.070	1.69	0.828	0.158	0.038	1.67

Table 2: Certificate values for lithium pegmatite ore reference materials analyzed in this study, in order of descending Li content.

<table>
<tr><th colspan="12">OREAS 750 Nano-Pellet</th></tr>
<tr><td>Measured Element</td><td>Li</td><td>Na</td><td>Mg</td><td>Al</td><td>Si</td><td>P</td><td>K</td><td>Ca</td><td>Ti</td><td>Mn</td><td>Fe</td></tr>
<tr><td>Mean wt. % (n=25)</td><td>0.234</td><td>1.57</td><td>0.31</td><td>5.15</td><td>36.82</td><td>0.064</td><td>1.8</td><td>0.824</td><td>0.154</td><td>0.04</td><td>1.76</td></tr>
<tr><td>Mean Recovery</td><td>1.01</td><td>1.02</td><td>0.99</td><td>0.95</td><td>1.00</td><td>0.92</td><td>1.07</td><td>0.99</td><td>0.97</td><td>1.04</td><td>1.05</td></tr>
<tr><td>RSD %</td><td>2</td><td>3</td><td>3</td><td>3</td><td>1</td><td>10</td><td>3</td><td>6</td><td>4</td><td>4</td><td>3</td></tr>
<tr><th colspan="12">OREAS 751 Nano-Pellet</th></tr>
<tr><td>Measured Element</td><td>Li</td><td>Na</td><td>Mg</td><td>Al</td><td>Si</td><td>P</td><td>K</td><td>Ca</td><td>Ti</td><td>Mn</td><td>Fe</td></tr>
<tr><td>Mean wt. % (n=25)</td><td>0.46</td><td>2.53</td><td>0.301</td><td>8.4</td><td>33.31</td><td>0.119</td><td>2.5</td><td>0.806</td><td>0.141</td><td>0.067</td><td>1.69</td></tr>
<tr><td>Mean Recovery</td><td>0.99</td><td>1.03</td><td>1.05</td><td>1.05</td><td>1.00</td><td>0.96</td><td>1.04</td><td>1.09</td><td>0.98</td><td>1.03</td><td>1.04</td></tr>
<tr><td>RSD %</td><td>2</td><td>2</td><td>2</td><td>2</td><td>1</td><td>9</td><td>2</td><td>2</td><td>4</td><td>3</td><td>2</td></tr>
<tr><th colspan="12">OREAS 752 Nano-Pellet</th></tr>
<tr><td>Measured Element</td><td>Li</td><td>Na</td><td>Mg</td><td>Al</td><td>Si</td><td>P</td><td>K</td><td>Ca</td><td>Ti</td><td>Mn</td><td>Fe</td></tr>
<tr><td>Mean wt. % (n=25)</td><td>0.704</td><td>2.8</td><td>0.047</td><td>8.45</td><td>34.24</td><td>0.134</td><td>2.17</td><td>0.218</td><td>0.015</td><td>0.082</td><td>0.893</td></tr>
<tr><td>Mean Recovery</td><td>1.01</td><td>1.03</td><td>1.08</td><td>1.06</td><td>1.00</td><td>0.95</td><td>1.04</td><td>1.10</td><td>0.94</td><td>1.04</td><td>1.07</td></tr>
<tr><td>RSD %</td><td>2</td><td>2</td><td>2</td><td>2</td><td>1</td><td>10</td><td>3</td><td>3</td><td>4</td><td>3</td><td>5</td></tr>
<tr><th colspan="12">OREAS 753 Nano-Pellet</th></tr>
<tr><td>Measured Element</td><td>Li</td><td>Na</td><td>Mg</td><td>Al</td><td>Si</td><td>P</td><td>K</td><td>Ca</td><td>Ti</td><td>Mn</td><td>Fe</td></tr>
<tr><td>Mean wt. % (n=25)</td><td>1.011</td><td>2.21</td><td>0.014</td><td>8.58</td><td>34.46</td><td>0.11</td><td>2.01</td><td>0.133</td><td>0.003</td><td>0.077</td><td>0.907</td></tr>
<tr><td>Mean Recovery</td><td>1.03</td><td>1.02</td><td>1.25</td><td>1.04</td><td>1.00</td><td>0.99</td><td>1.04</td><td>1.18</td><td>0.85</td><td>1.04</td><td>1.08</td></tr>
<tr><td>RSD %</td><td>2</td><td>2</td><td>3</td><td>3</td><td>1</td><td>18</td><td>2</td><td>11</td><td>3</td><td>2</td><td>5</td></tr>
</table>

Table 3: Mean recovery ratio (Measured Mean/Reference Value = 1.01 = 101%) and relative standard deviation % (Standard Deviation/Measured Mean) for secondary reference materials measured by LA-ICP-MS.

The worst outcomes were for Mg, Ca, and Ti in OREAS 753, which exhibited recovery of 125%, 118%, and 85%, respectively. All other elements in all reference materials recovered within 10% of the reference value. RSD% was less than 5% for all elements in all reference materials except for P which was 10% or less in OREAS 750–752 and 18% in OREAS 753.

Measurement of P in future work may benefit from the use of Triple Quadrupole (MS/MS) mode with oxygen mass shift such that P is measured off-mass as $^{31}\mathrm{P}^{16}\mathrm{O}$. This approach was not pursued in this study because LA-ICP-MS is only compatible with a single collision-reaction cell mode because of its time resolved nature; switching between gas modes could result in a failure to collect representative data in a sample with any measurable heterogeneity. If P measurement is improved by an oxygen mass shift, future work may explore adding S as analyte since it too can be measured off-mass as $^{32}\mathrm{S}^{16}\mathrm{O}$. This would avoid oxygen dimer interference at mass 32 and isobaric interference from $^{48}\mathrm{Ti}$ if measured in MS/MS mode which would filter out $^{48}\mathrm{Ti}$ prior to a mass shift reaction.

GDMS was originally developed for measuring trace impurities in conductive, high purity metals. Here, GDMS is used as a survey technique for measuring trace impurities in the five nanopowdered reference materials (four Li ores, OREAS 750–753, and one Li concentrate, OREAS 999) to determine its viability as an analysis technique for nonconductive mixed oxide material. Commercially, this would be part of a "full scan" analysis suite in which LA-ICP-MS measures the major and minor elements as described above. GDMS can quantify elements down to sub-ppm levels in these complex materials, with 47 of 54 elements being within a factor of two of the reported concentrations (certified and informational). GDMS is used here as a standard-less (uncalibrated) technique, relying on fixed RSFs developed experimentally for non-conductive oxides. The absence of empirical calibration raises the issue of stability of the technique across different instruments. However, 45 of the 54 elements exhibit 25% or lower RSD% variability across the different reference materials while analyzing them using multiple Astrum ES instruments; this illustrates the reproducibility and stability of GDMS in the absence of reference material calibration. The ability to perform direct analysis of the solid material without chemical preparation allows for faster, safer, and more efficient analysis than solution ICP-MS. GDMS's stability and low reporting limits make it a powerful tool for supply-chain integrity by elemental "fingerprinting" of ore bodies, as well for as purity analysis of Li-ore and concentrates.

	MEAN RECOVERY RATIO					
ELEMENT	OREAS 750	OREAS 751	OREAS 752	OREAS 753	OREAS 999	INTER-SAMPLE VARIANCE*
Li	1.36	1.08	1.00	0.99[a]	0.96[a]	15%
Be	1.79	1.89	2.04	2.01	2.00	5%
B	-	1.45[b]	0.33[b]	1.07[b]	-	60%
Na	1.09[a]	0.94[a]	0.83[a]	0.89[a]	1.03	11%
Mg	1.41	1.31	1.34	1.65	1.27	11%
Al	1.26[a]	1.17[a]	1.04[a]	1.06[a]	1.14[a]	8%
Si	0.89[a]	0.91[a]	0.96[a]	0.97[a]	0.94[a]	4%
P	1.78	1.86	1.94	2.06	1.83	6%
S	1.80	2.02	2.23	2.41	1.91	12%
Cl	0.58[b]	0.47[b]	0.63[b]	0.72[b]	-	17%
K	1.46[a]	1.25[a]	1.21[a]	1.04[a]	1.46	14%
Ca	1.51	1.32	1.19	1.41	1..33	9%
Sc	1.47	1.34	1.14	1.13	151	14%
Ti	1.44	1.34	1.26	1.13	1..40	9%
V	1.34	1.15	1.15	1.26	1.22	7%
Cr	1.27	1.99	0.71	1.72	1.46	34%
Mn	1.26	1.14	1.08	1.11	1.14	6%
Fe	1.04[a]	1.02[a]	1.11	1.12	1.06[a]	4%
Co	1.03	1.02	0.97	0.94	1.04	4%
Ni	1.13	1.01	1.00	1.05	0.95	7%
Cu	0.90	0.91	0.82	0.78	0.94	8%
Zn	1.13	1.13	1.18	1.42	1.18	10%
Ga	1.31	1.06	0.90	0.80	0.92	20%
Ge	0.84	0.90	0.84	0.81	0.85	4%
Rb	2.00	1.87	1.61	1.34	1.58	15%
Sr	1.81	1.64	1.22	1.21	1.28	19%
Y	2.18	2.05	1.80	1.83	1.94	8%
Zr	5.43	1.48	1.35	1.33	1.50	81%
Cd	0.69	0.71	0.67	1.42	1.81[b]	49%
Sn	1.04	1.00	0.90	0.94	1.00	5%
Sb	0.46	1.10	0.51	0.42	0.53	47%
Te	-	2.18[b]	0.28[b]	0.44[b]	1.69[b]	81%
Cs	1.89	1.69	1.51	1.04	1.44	21%
Ba	1.71	1.54	1.41	1.34	1.62	10%
La	2.18	1.99	1.96	1.86	2.33	9%
Ce	2.10	1.96	196	1.70	2.13	9%
Pr	2.01	1.83	166	1.39	1.89	14%
Nd	2.00	1.92	1.75	1.34	1.83	15%

*Table 4: Inter-sample variability and mean recovery ratio of the OREAS Li pegmatite suite and Li concentrate. [a]For elements over 1 wt. % concentration, recovery is shown for information only because these elements are normally reported as "matrix". [b]Indicative value only from certificate. *Inter-sample variance is the relative standard deviation of mean recovery ratio for a given element across the five reference materials. Table continued on next page.*

	MEAN RECOVERY RATIO					
ELEMENT	OREAS 750	OREAS 751	OREAS 752	OREAS 753	OREAS 999	INTER-SAMPLE VARIANCE*
Sm	1.91	1.83	1.52	1.68	1.73	9%
Eu	1.81	1.78	1.41^{b}	-	1.69^{b}	11%
Gd	2.76	2.50	2.24	1.82	2.10	16%
Tb	2.29	2.06	1.54	1.36^{b}	0.18	21%
Dy	1.98	1.74	1.61	1.49	1.67	11%
Ho	1.72	1.59	1.52	2.14	1.55	15%
Er	1.79	1.47	1.55	1.64	1.47	8%
Tm	1.84	1.69	0.87^{b}	-	1.75^{b}	29%
Yb	1.63	1.87	2.25^{b}	-	2.61	21%
Lu	2.06	2.54	1.23^{b}	-	1.98^{b}	28%
Hf	6.75	4.07	2.45	3.01	2.38	49%
Tl	0.83	0.74	0.84	0.96	0.76	11%
Pb	1.33	0.92	1.06	1.13	1.11	13%
Bi	0.94	0.69	0.84	0.99	0.93	13%
Th	1.82	1.67	1.73	1.77	1.81	4%
U	1.85	1.74	1.64	1.66	1.82	5%

Table 4: Continued from previous page.

Future work required to further validate this approach will entail re-analysis of the OREAS reference materials as non-nanopowder pressed pellets. The nanopowders exhibited ablation behavior more similar to a cohesive solid than to a typical pellet made from a bulk rock powder. In this study, the maximum laser spot diameter possible with the ESL imageGEO 193 (150 µm) was used. If non-nanopowder pellets contain mineral grains greater in size than the spot diameter of the laser, then much greater RSD% may be anticipated. Creating nanopowders for all routine commercial samples of spodumene ore is not a viable option, but it may be possible to obtain more representative results in a non-nanopowder by creating a large pellet and using a raster ablation to analyze a substantial greater area per sample than the scan lines used in this study. Similarly, GDMS only requires approximately 10 mg of material for analysis, which can result in non-representative results if the powder is not homogenized. Additionally, re-analysis of the OREAS references materials will also entail using Si content measured by portable X-Ray Fluorescence (pXRF) or Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) for internal standardization of LA-ICP-MS results, since reference values will of course be unavailable for commercial samples of unknown composition.

REFERENCES

1. McKinsey & Company. (2023). Battery 2030: Resilient, sustainable, and circular. [White Paper] https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular
2. Pioneer Resources Limited. (2016). Pioneer Announces A 5,000M RC Drilling Programme At Its Pioneer Dome Lithium Project, WA. [White Paper] https://announcements.asx.com.au/asxpdf/20160727/pdf/438tzhbng6pwv9.pdf
3. Bartov, G., and Putyera, K. New Oxide-Specific RSFs to Improve Non-Conductive Oxide Materials Analysis by GDMS. Application Note. https://www.eag.com/app-note/rsf-to-improve-analysis-by-gdms/