

Lithium analysis of brines and minerals for exploration and resource definition

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Introduction

Lithium has been dubbed “white petroleum” by the media, vying with copper to become the “new oil”, as electricity from renewable power substitutes for fossil fuels in the coming energy transition where internal combustion engines will be replaced by electric motors. Car manufacturers are quickly increasing production of electric vehicles, many planning to be totally electric over the next dozen years (Volkswagen 2020). Lithium is the primary choice for electric car batteries as it is lightweight, has a high energy density and can be repeatedly recharged. Gigafactories have been constructed for the manufacture of lithium batteries in the US, China and Europe. Lithium-ion batteries are also the battery of choice for grid storage electricity from renewable sources. This, in turn, has ramped up demand for lithium, with production doubling over the past decade to the extent that lithium usage for rechargeable batteries constituted 56% of total lithium consumption (Kavanagh *et al.* 2018). This dwarfs its previous industrial usage for greases, ceramics and in medical applications (Bibienne *et al.* 2020).

While prices for lithium have fluctuated in the past few years, a recent trend tracked by S&P Global Market Intelligence (2022) shows that Chinese battery-grade lithium carbonate prices have risen by 500% since mid-2020 to early 2022. This has driven production and investment in the industry; financings for new lithium and specialty commodity projects are at an all-time high of almost \$6 billion in 2021 with the prospect of demand doubling within the next three years (Fig. 1).

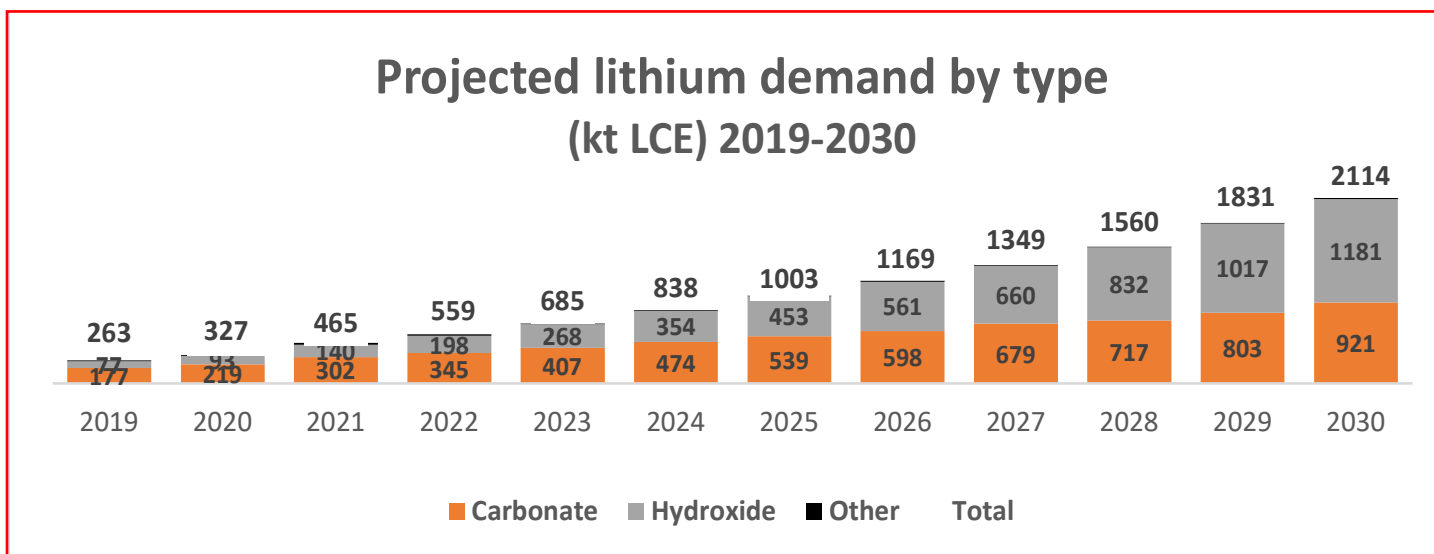


Figure 1. Global projected lithium demand (kt Lithium Carbonate Equivalent (LCE)) to 2030 (Cochilco 2022)

Lithium is produced from two main sources: low-grade lithium brines, and pegmatite deposits that represent concentrated sources of lithium (Kesler *et al.* 2012). Australia is the largest global producer at 40,000 tonnes of the 82,000 tonne global lithium production, mostly from pegmatite resources in Western Australia (USGS 2021). Other sources of lithium include: volcanic clay deposits, where lithium occurs within clay minerals such as hectorite; loosely held adsorbed lithium ions in clay minerals; and the unique jadarite (a lithium silicate borate) -bearing volcano-sedimentary deposits in the Jadar valley in Serbia (Bowell *et al.* 2020). This deposit could provide 10% of global Li demand were it to be developed. New development projects are equally divided between brines and hard rock sources (Fig. 2), but 81.8% of new lithium production will come from hard rock sources (S&P Global Market Intelligence 2022).

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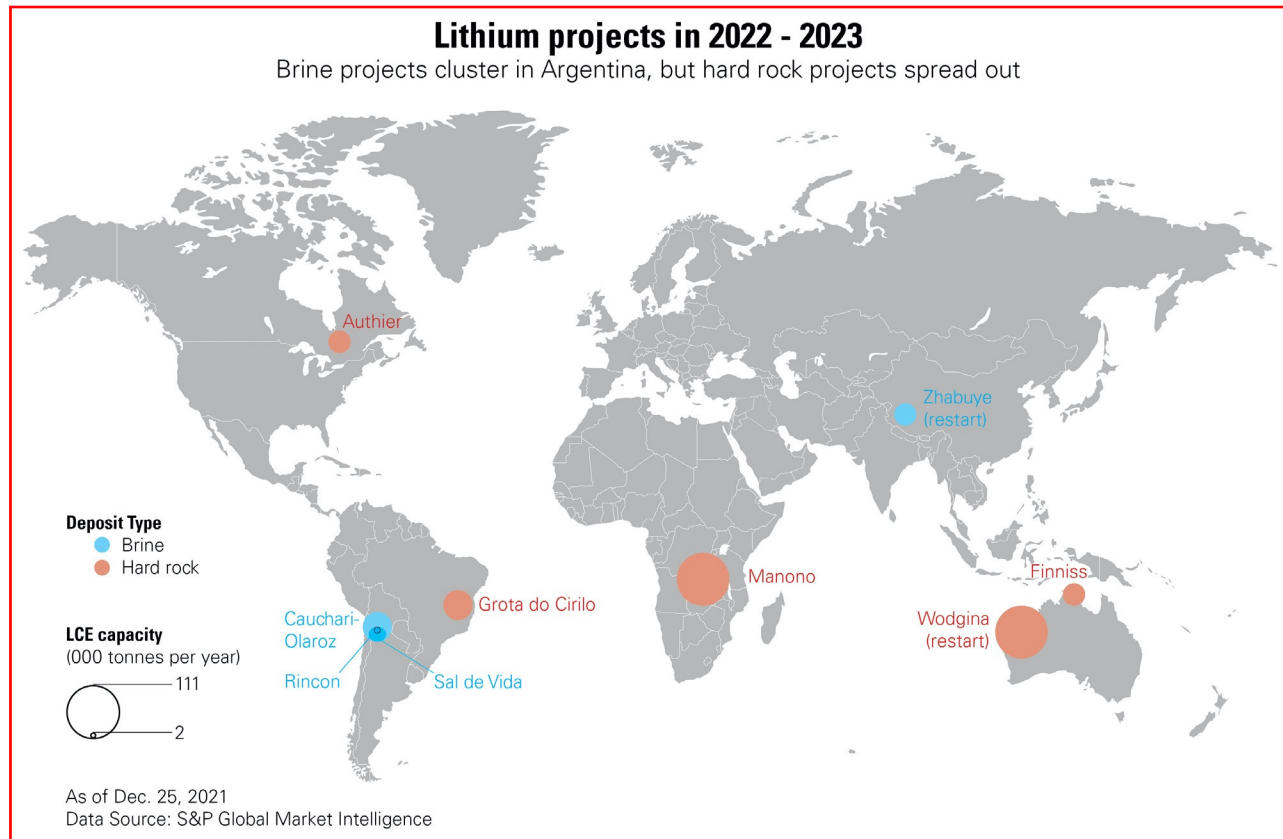


Figure 2. New lithium projects, five hard rock and four brine projects - spodumene projects will account for 81.8% of the expected 355,000-tonne LCE capacity increase (S&P Global Market Intelligence 2022).

Lithium brine deposits represent approximately 70% of global lithium reserves and occur mainly in salars in the Lithium Triangle in South America where the borders of Bolivia, Argentina and Chile meet (Munk *et al.* 2016). As indicated by Bowell *et al.* (2020), lithium brines are hypersaline fluids with salinities between 1.7 and 24 times that of seawater. Lithium is concentrated after a long solar evaporation period of between 12 to 24 months, followed by chemical methods to extract lithium compounds. Lithium production from brine sources is estimated to be about 40% of global production mainly from the Lithium Triangle (USGS 2021).

Properties

Lithium is the third element in the periodic table and belongs to the alkali metal group. It is the least dense solid element with a density of 0.534 g/cm³, about half that of water. Lithium is highly reactive with a single valence electron that is easily lost to form a small cation, allowing it to substitute in a wide range of minerals. Hofstra *et al.* (2013) have indicated that lithium's small ionic radius and +1 charge enables it to have a much higher diffusion rate compared with other alkali metals. This property may allow lithium to migrate from lithophile element enriched rhyolitic tuffs, to form brines in enclosed terrestrial basins. It may also help produce surface

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soil anomalies in transported materials over buried pegmatites as discussed below.

Lithium has a very low ionization energy compared with other alkali metals, and is easily excited for atomic emission spectroscopy, atomic absorption spectroscopy (AAS) or inductively coupled plasma – atomic emission spectroscopy (ICP-AES). In a flame, lithium compounds and minerals have a characteristic crimson colour that is very recognisable in flame blowpipe tests (Read 1970). Lithium is also easily excited by a laser which is the basis for laser-induced breakdown spectroscopy (LIBS) instruments.

Under X-ray irradiation, lithium emits a very low energy K alpha line at 54 eV that can only be detected by specialized X-ray detectors (Burgess *et al.* 2013). This means that lithium cannot be detected by laboratory X-ray fluorescence (XRF) energy dispersive or wavelength dispersive instruments or by portable XRF systems. Although this may be considered unfortunate, it has allowed the widespread use of lithium metaborate/tetraborate flux mixes for preparing homogenized glass disks for whole rock analysis by XRF and other spectroscopic methods. In geochemical laboratory design, an important consideration should be the isolation of labs using lithium fluxes from those areas carrying out digestions for lithium determination.

Another consequence of lithium producing only a weak X-ray is that lithium-bearing minerals cannot be completely identified in electron beam instruments used for automated mineralogy, such as QEMSCAN, MLA or TIMA-X, since these techniques rely on energy dispersive X-ray spectrometry to measure mineral chemistry. Instead, alumino-silicate ratios and other elemental data are used to identify the various lithium-bearing minerals and determine their modal abundances. Because the lithium grade alone does not directly correspond to the overall value of an ore body, these modal abundances are important in understanding lithium deportment in pegmatites in order to assess the mineral resource. Its value is determined instead by the proportion of lithium minerals that can be sold to the higher priced battery markets. This problem has provided the impetus to develop alternate lithium mineral quantification methods such as the use of Fourier Transform Infra-Red spectroscopy (FTIR) discussed below.

Lithium in minerals cannot be determined by the wavelength dispersive X-ray detectors in electron probe microanalysis systems commonly used for quantitative determination of mineral chemistry. However, the development and widespread use of laser ablation inductively coupled plasma – mass spectrometry (LA-ICP-MS) systems has alleviated this situation in recent years; ICP-MS uses atomic mass to measure elemental abundance.

Analysis of lithium brines

The lithium content of brines is best determined by ICP-based techniques rather than AAS due to their ability to measure other elements of interest simultaneously. The high level of total dissolved solids (TDS) in brines (typically 5-15% TDS) does pose an issue as the high salt content can quickly clog nebulizers and cones in ICP instrumentation and burner apertures in AAS instruments (Potts 1992). Pre-dilution of the brine samples and humidifiers for the carrier gas can lessen the salt content entering the plasma or flame. A second issue is that the high salt content increases the background and matrix interferences, causing a rise in detection limits. However, there are no significant spectral interferences for lithium using either ICP-AES, due to its high emission wavelengths, or ICP-MS because of its low mass.

Typical lower detection limits (LDLs) for lithium in brines are 2-10 mg/L by ICP-AES and 0.01 mg/L by ICP-MS compared to LDLs of 0.01 mg/L and 0.0001 mg/L, respectively in groundwaters with low TDS. ICP-MS methods would be required to determine lower levels of lithium in groundwaters, geothermal brines or oil field brines, where concentrations can be between 0.1 and 700 mg/L (Kavanagh *et al.* 2018).

Lithium in minerals

Volcanic clay lithium deposits, such as those found in Nevada, where lithium occurs in the clay mineral hectorite, or as an inter-layer cation, or absorbed on clay mineral surfaces, are easily analysed for lithium and multi-element packages

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using a four-acid digestion (a mixture of hydrofluoric, perchloric, nitric and hydrochloric acids). It might be expected that aqua regia digestion would extract all the lithium from such mineral hosts, but it is not recommended since there are some indications that aqua regia digestions extract slightly less lithium than four-acid digestions (Hilsher *et al.* 2021). However, jadarite is easily dissolved in mineral acids for the determination of lithium and other elements (Stanley *et al.* 2007).

Rare element granitic pegmatites are currently the main source of lithium from hard rock ores. They are also the source of metals such as Be, Rb, Cs, Ta, Nb, Sn, and the rare earth elements. Granitic pegmatites are widespread, but the rare metal pegmatites make up less than 1% of this group and lithium-bearing pegmatites are an even smaller proportion (Kesler *et al.* 2012; London 2016; Howell *et al.* 2020). These rare element granitic pegmatites are further sub-divided into Lithium-Caesium-Tantalum (LCT) and Niobium-Yttrium-Fluoride (NYF) families (Černý 1991), with the former being the main source of lithium. The mineralogy of the rare element granitic pegmatites can be very complex, for example, 44% of the 124 lithium-bearing minerals known to exist occur in LCT pegmatites (Grew 2020). Of these, the key minerals for lithium extraction are spodumene, petalite and lepidolite, with spodumene being the most important ore mineral currently mined.



Figure 3. Lithium-Caesium-Tantalum (LCT) pegmatite showing metre-sized white spodumene crystals with quartz, albite and petalite. M.A. Laporte, SGS Geological Services.

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Analysis of spodumene-bearing pegmatites for lithium is challenging because it appears to be a highly refractory mineral that does not readily dissolve in four-acid digestions using methods followed by commercial laboratories. Aqua regia (nitric and hydrochloric acid) is clearly not strong enough since it lacks the hydrofluoric acid that is key to breaking down silicates. This leaves the fusion methods as alternatives, but lithium metaborate fusions have to be excluded for obvious reasons, leaving sodium peroxide fusion as the only method available for spodumene-bearing ores. Laboratory observations indicate that sodium peroxide fusion methods have a higher recovery of lithium than four-acid digestions. For example, in the OREAS reference material database, OREAS 753 is an LCT pegmatite with coarse spodumene and is certified at 1.02% Li using peroxide fusion ICP-AES versus 0.985% Li with four-acid digestion (<https://www.oreas.com/crm/oreas-753/>). An analysis of a large geochemical database for an LCT pegmatite shows a consistent underestimate of Li content by four-acid digestion of approximately 4% (Yann Camus pers. comm.). A similar trend is seen in aluminium content which is the other major element besides silicon in spodumene. Silicon is volatilized during four-acid digestion as SiF₄ and cannot be determined. However, other lithium-bearing minerals in LCT pegmatites appear to dissolve well in four-acid digestions. In summary, sodium peroxide fusion is the preferred method because it decomposes all of the pegmatite, including refractory minerals such as tourmaline, zircon, cassiterite and garnet.

Li in surficial geochemical exploration

Many of the lithium-bearing mineral species, other than spodumene and tourmaline, are likely to break down in the surficial environment and release their ions. As we have seen from the concentrations in brines, lithium is a highly mobile element and likely to disperse upward and outward from LCT pegmatites. Galeschuk and Vanstone (2007) indicated that geochemical methods for discovery of buried LCT pegmatites are essential because these bodies are not responsive to geophysical methods. Downhole litho-geochemical methods clearly show a lithium halo around the pegmatite, while surficial soil geochemistry using the Enzyme Leach method shows weak apical anomalies for Li and Ta as well as haloes for Rb and Cs. Studies conducted using the Mobile Metal Ion (MMI) method for surficial soils over buried LCT pegmatites show clear Li, Cs and Rb surficial responses at the Thompson Brothers property in the Snow Lake area of Manitoba, Canada (SGS 2017) and they led to the discovery nearby of the high-grade D8 spodumene-bearing pegmatite on the Zoro property of Foremost Lithium Resource and Technology (Grammatikopoulos et al. 2020). More recent work using MMI on vegetation at a property near Leaf Rapids in northern Manitoba indicates good Li, Cs and Ta responses over a buried LCT pegmatite (M. Fedikow, pers comm 2021).

One benefit of refractory spodumene, as referred to by Černý (1991), is that it may serve as an important indicator mineral for the very rare LCT pegmatites in the same way as G10 garnets are for diamond-bearing kimberlites. The hardness of the mineral and its resistance to chemical breakdown would ensure its survival in glacial till and stream sediment dispersion trains. With a specific gravity (SG) of 3.15, it would be recovered in the mid-density mineral fraction as SG >3.2 is the standard threshold between light and heavy fractions in indicator mineral processing of sediment samples. As mentioned previously, a sodium peroxide fusion-based method would be the preferred analysis for these sediment samples. If portable instrumentation were available, portable LIBS would be the recommended instrument for lithium analysis.

FTIR analysis of Pegmatites

FTIR spectroscopy is an established method for determining qualitative mineral identification based on an infrared spectrum of absorption or emission (Griffiths and de Hasseth 2007). It is similar to X-ray diffraction (XRD) in that it identifies and quantifies a wide range of minerals, but based on molecular vibrations and rotations from specific bonds. The Bruker Alpha II unit collects high-spectral-resolution data over a wide range from 500 – 4000 cm⁻¹ with a resolution of 4 cm⁻¹ in attenuated total reflection (ATR) mode based on a diamond system ideal for minerals which have a high hardness

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index. FTIR provides a low-cost rapid solution with a two- minute analysis time for pegmatite mineral analysis without the need for complex sample preparation. It uses standard analytical pulps for analysis. Calibration and validation details are discussed in Woods (2019). The calibration graphs for Li and spodumene are displayed in Figure 4 and the range of minerals determined is shown in Table 1. The Li and Ta analysis may be considered a chemometric measurement where these elemental data are derived from predictive modelling generated from FTIR data using machine learning techniques indicating not only lithium content but its distribution in spodumene and in micaceous phases.

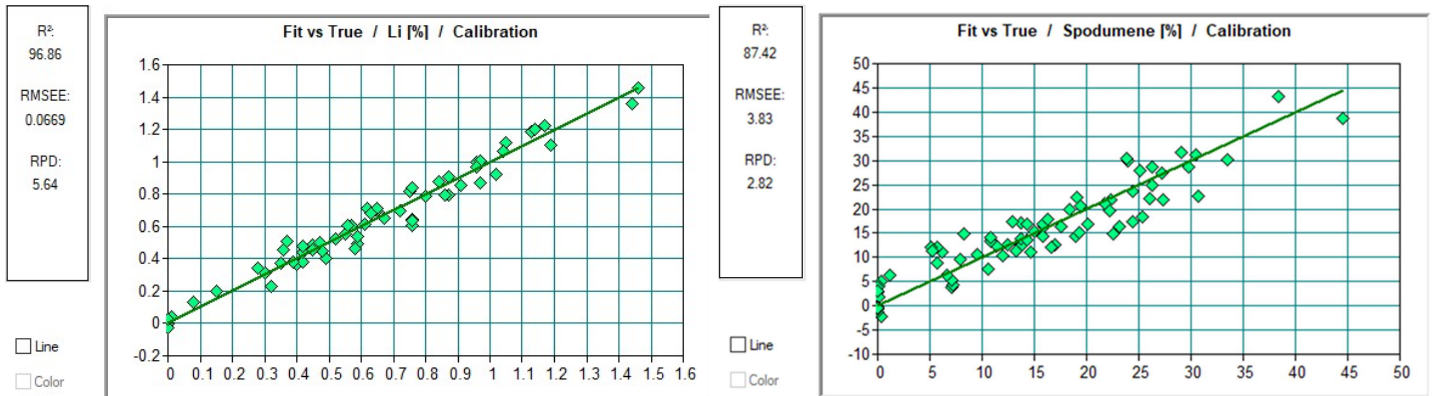


Figure 4. Calibrations developed for Li and spodumene analysis by FTIR by SGS Perth (Woods 2019).

| Mineral | | Range | | Mineral | | Mineral | | Mineral | |
|---|--|-------|-------|---------------|------|---------|------------|---------|-----|
| | | From | To | | | | | | |
| Apatite | | 1.0 | 70.0 | Quartz | 1.0 | 100.0 | Total TiO2 | 1.5 | 3.5 |
| Calcite | | 1.0 | 100.0 | Siderite | 1.0 | 30.0 | | | |
| Chlorite | | 1.0 | 100.0 | Smectite | 1.0 | 100.0 | | | |
| Dolomite | | 1.0 | 100.0 | Spodumene | 1.0 | 100.0 | | | |
| Goethite | | 1.0 | 20.0 | Biotite | 1.0 | 60.0 | | | |
| Illite | | 1.0 | 100.0 | Muscovite | 1.0 | 40.0 | | | |
| K Feldspar | | 1.0 | 50.0 | Tantalum | 1.0 | 45.0 | | | |
| Kaolinite | | 1.0 | 100.0 | Total Alumina | 20.0 | 60.0 | | | |
| Petalite | | 1.0 | 40.0 | Total FeOxide | 3.0 | 30.0 | | | |
| Plagioclase | | 1.0 | 100.0 | Total Silica | 1.0 | 35.0 | | | |
| FTIR with ATR on Pulp scan with quantification on generic BULK mineral setup. | | | | | | | | | |
| all IR active minerals normalized to 100% | | | | | | | | | |

Table 1. Mineral calibrations developed for the Bruker Alpha II FTIR system used in pegmatite and other projects (Woods 2019).

Portable systems

As noted, lithium does not emit a measurable X-ray that can be detected by portable X-ray systems although Brand & Brand (2017) and Brand *et al.* (2020) have developed an algorithm to estimate lithium content in LCT pegmatites using pXRF data from other elements in a pegmatite sample.

Laser-induced breakdown spectroscopy (LIBS) uses an intense laser to generate emissions and can measure lithium in solid samples. Both LIBS and portable LIBS (pLIBS) have been used for assaying pegmatite-derived exploration, grade control and production samples. The assays are carried out on pressed pellets of the analytical grade using reference materials and samples analysed by other techniques for calibration. Lithium and other major elements such as Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn and Fe can be determined simultaneously. Accuracy and precision are limited by sample preparation, but initial data show they are comparable to pressed pellet pXRF. As an added feature, the spatially resolved Li signal from the pellet can be used to evaluate homogeneity of the preparation. Portable LIBS instruments, with their lower power, analyse a smaller area than benchtop units and are more suited to early stage exploration due to their inferior precision and accuracy. LIBS applications look promising and will benefit from more comparison with AAS- and ICP-based assays.

Our group has also carried out several studies to test the ability of core scanning systems to detect lithium and lithium minerals. For elemental scanning, LIBS-equipped scanning systems are under investigation to characterise lithium distribution as lithium is not detected by XRF based sensors. Hyperspectral scanning using VNIR-SWIR cameras cannot

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easily detect lithium-bearing minerals in pegmatite. The goal is that scanning systems equipped with LWIR or FTIR cameras will be able to detect these minerals such as spodumene, petalite and lepidolite.

Conclusions

As the effort to replace fossil fuels gathers pace lithium is rapidly becoming a leading industrial resource because of its physical properties that make it suitable for battery storage and one that would not be easily replaced by other metals. The concern is whether there are sufficient lithium resources available to meet the demand for the metal. In this, proper lithium analysis in the exploration and resource definition of lithium sources is critical, particularly for the analysis of spodumene-bearing hard rock resources where sodium peroxide fusion is currently the only viable digestion method for complete recovery of lithium. Developing portable system technologies such as FTIR and LIBS will be central to field-based analytical schemes for lithium.

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