Laser-induced breakdown spectroscopy (LIBS) as a tool for in situ mapping and textural interpretation of lithium in pegmatite minerals

MARCUS T. SWEETAPPLE¹,* AND STEVEN TASSIOS²

¹CSIRO, Earth Science and Resource Engineering, P.O. Box 1130, Perth, Western Australia 6102, Australia
²CSIRO, Process Science and Engineering, Gate 1, Normanby Road, Clayton, Victoria 3169, Australia

ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) offers an efficient method for qualitative and semi-quantitative analysis of light elements ($Z < 10$), including lithium. This relatively inexpensive analytical tool provides very rapid analysis with little sample damage, requiring minimal sample preparation. In principle, LIBS is a form of atomic emission spectroscopy, relying on characteristic spectra emitted from plasma generated by a high-energy laser pulse striking a sample (solid, liquid, or gas).

In this study, LIBS mapping was applied to petrographically characterized samples of hydrothermally altered spodumene from the Neoarchaean Mt. Cattlin lithium pegmatite deposit. Spodumene (LiAlSi$_2$O$_6$) is the ore mineral in this deposit, but lithium is distributed in variety of minerals including primary micas and tourmaline, as well as in the alteration mineralogy of spodumene. Mapping was carried out using a grid of analysis spots of 125 μm diameter, spaced at 200 μm intervals, on a sample surface cut by a diamond saw blade without further preparation. Results from mapping of lithium in these samples effectively discriminated between spodumene, its alteration mineralogy, and matrix silicate minerals of the matrix. However, quantification of LIBS results using lithium-doped borosilicate glasses as standards was limited due to issues with the sensitivity of matrix matching of standards and self-absorption effects at Li$_2$O values greater than ~2 wt%, especially at values greater than ~6 wt%. The results of this study testify to the effectiveness of LIBS as a mapping tool for light elements, which may be used as a complement to other mapping techniques. Mapping of lithium in pegmatite minerals has important applications in exploration, evaluation, and beneficiation of lithium pegmatite ore bodies.

Keywords: Lithium, pegmatite, LIBS, mineral mapping, laser-induced breakdown spectroscopy

INTRODUCTION

Lithium is a problematic element for in situ mineral analysis by most routine microanalytical techniques available to geoscientists. For example, it cannot be detected or analyzed as part of routine element suites by energy-dispersive spectroscopy (EDS) and electron microprobe analysis (EMPA) because its wavelength lies outside the accessible range for current instrumentation, due to absorption of its low-energy characteristic X-ray emission line (e.g., Reed 2005). Other techniques such as ion or proton microprobe, electron energy loss spectroscopy (EELS), and secondary ion mass spectrometry (SIMS), and laser-ablation ICP-MS, which can provide effective lithium analysis, may be difficult to access or impracticable, and may also be expensive. These drawbacks are particularly true in industrial contexts relating to exploration for, and mining and processing of, lithium minerals, where Li content is typically evaluated purely by bulk chemical analyses.

In the case of rare metal granitic pegmatites, particularly the LCT petrogenetic type of Černý (1993) and Černý and Ercit (2005), lithium may be distributed across several different mineral species within the same pegmatite, both those having Li as an essential component, such as petalite (LiAlSi$_2$O$_6$), spodumene (LiAlSi$_2$O$_6$), and amblygonite-montebrasite [LiAl(PO$_4$)(F,OH)], and those minerals having variable amounts of Li substitution, such as di- and trioctahedral micas and tourmaline. The sheer complexity of mineralogical assemblages of granitic pegmatites, combined with the varying stages of primary, secondary, and alteration mineral paragenesis may result in wide ranges of mineralogical and textural variation in lithium distribution in rare metal granitic pegmatites. Such issues become of paramount importance in the interpretation of Li data obtained from whole rock analyses in the aforementioned industrial context. Characterization of distinct Li species is essential when ore beneficiation processes are designed to recover minerals with distinct physical properties such as specific gravity.

The most common approach to obtaining an estimate of lithium content of minerals from microanalytical data is by calculations from quantifiable elements from EMPA data, making use of well-known structural formulas derived from measurable major and minor elements. These calculations typically require normalization, charge balance and/or difference calculations based on other atomic species, or in the case of micas make use of empirical relationships between Li and other elements, such as Mg, F, and Si (e.g., Monier, and Robert 1986; Tindle and Webb 1990; Tischendorf et al. 1997, 1999). However, all of these calculations are invariably limited by inherent assumptions regarding the extent of site occupancy, presence of site vacancies, substitution relationships, and the oxidation state of iron. A discussion of some different