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**DETERMINATION OF $^7\text{Li}/^6\text{Li}$ ISOTOPE RATIOS
IN GEOLOGICAL MATERIALS
BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**

by

Barbara M. Acheson, B.Sc.

**A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science**

Ottawa-Carleton Geoscience Centre

and

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**DETERMINATION OF $^7\text{Li}/^6\text{Li}$ ISOTOPE RATIOS IN GEOLOGICAL
MATERIALS BY INDUCTIVELY COUPLED PLASMA MASS
SPECTROMETRY**

submitted by Barbara M. Acheson, B.Sc.
in partial fulfilment of the requirements
for the degree of Master of Science

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January 5, 1995

ABSTRACT

A method for the determination of Li isotope ratios in a variety of Li-minerals using Inductively Coupled Plasma Mass Spectrometry is described. Lithium isotope ratios are determined with a precision of better than 0.1% and with an absolute accuracy of greater than 0.6% in samples containing as little as 60 ppb Li. Sample material is digested with HF and HCl in sealed Teflon vials and then Li is separated from the matrix on Bio-Rad AG50W-X8, 100-200 mesh cation exchange resin, since concomitant elements in solution are shown to cause isotope ratio shifts at concentrations above 100 ppm for several elements (Na, K, Ca, Cs, Sr, Mg). The measured isotope ratios ($^7\text{Li}/^6\text{Li}$) in individual minerals yielded $\delta^6\text{Li}$ values relative to the reference Li_2CO_3 standard IRM-016 (IRM-016 has an absolute ratio of 12.29 ± 0.02) that ranged from +3 ‰ for lithiophorite from North Mountain Mine, Arkansas, to -33 ‰ for amblygonite from Tanco Mine. Analyses of five micas from topaz granites of two discrete geochemical types showed that lithium isotope ratios are slightly lower for peraluminous granites with high phosphorous contents, than for metaluminous granites with lower phosphorous contents, and that the lithium isotope ratios vary inversely to the $^{18}\text{O}/^{16}\text{O}$ isotope ratio of the whole rock samples.

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Finally, I would like to dedicate this thesis to three people that have gone on their journey since I started; my beloved grandfather, John William Bell whose face and smile I will never forget, my grandmother and best girlfriend, Evelyn Gertrude Snelgrove Bell, and my grandfather Harry Ross MacDougall Acheson, the man I admired and respected more than anyone. They weren't around to see me finish this, but they all knew I would.

ORIGINAL CONTRIBUTION

All sample preparation, procedure development (for both ion exchange and ICP-MS), ion exchange separations, lithium isotope ratio measurements and lithium concentration determinations were performed by the author. The electron-microprobe analyses were performed by Peter Jones at Carleton University and the oxygen isotope data used in Chapter 7 was provided by R.P. Taylor. Samples were supplied by The Canadian Museum of Nature, Dr. R.P. Taylor, Dr. J. Melgarejo, Dr. J. Van Velthuisen, and George Robinson. Lithium analyses were performed at the Geological Survey of Canada in the lab of Dr. D.C. Gregoire, and all other lab work was performed at Carleton University in the lab of Dr. R.P. Taylor.

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PREFACE

It is interesting to note that since 1910, less than 50 papers have been published on the subject of lithium isotope ratios. The majority of papers prior to 1963 were concerned primarily with performing atomic mass determinations for lithium. Between 1963 and the late 1970's, the main focus of lithium isotope studies was meteorites. Until 1993, only five studies had been published that dealt with the measurement of lithium isotope ratios for terrestrial geological samples. These five studies combined, contributed less than 65 lithium isotope ratio values to the literature, and all five of these studies used thermal ionization mass spectrometry as the analytical method. To date, ICP-MS has not been used to study lithium isotope ratios in geological materials, and it has been reported only twice in the literature as the analytical method for measuring lithium isotope ratios in biological materials; in both cases, achieving precisions no better than 1 %. The work described in this thesis, therefore, is the first study which successfully measures lithium isotope ratios with ICP-MS. Furthermore, this study contributes 55 lithium isotope ratio values to the data pool, nearly doubling the data collected for terrestrial materials in the last 25 years. Finally, this study is the only study of lithium isotope ratios of felsic rocks ever performed.

**PART I - ANALYTICAL METHOD FOR MEASURING LITHIUM
ISOTOPE RATIOS IN GEOLOGICAL MATERIALS**

CHAPTER 1

PART I - INTRODUCTION

Lithium is a geochemically important element that participates in a wide variety of geological processes (Heier and Billings, 1970). The element possesses two stable isotopes ${}^6\text{Li}$ (mass 6.00814 amu) and ${}^7\text{Li}$ (mass 7.00969 amu) (masses calculated from tables given in Lamberty et al, 1992), giving a relative mass difference of greater than 15 % between the two isotopes. The relative abundances of ${}^6\text{Li}$ and ${}^7\text{Li}$ are approximately 7.5 % and 92.5 % respectively. Differences in the physicochemical behaviour of isotopes result from the dependence of the momenta and kinetic energies of the nuclei on their masses (Karplus and Porter, 1970). As a result of this, and due to the relatively large mass difference between its isotopes, lithium will be a candidate for isotopic fractionation in nature. A number of mechanisms are responsible for isotopic fractionation in nature. Such processes as adsorption/desorption, melting/crystallization, diffusion, and ion exchange may all have an effect on the lithium isotope composition of geological materials. These processes are likely to be involved in such events as weathering, magma fractionation, partial melting and metasomatism.

Because of its low mass, lithium determinations have proven to be problematic. For example, lithium cannot be detected by any means involving emission of X-rays. The techniques of X-ray fluorescence, energy-dispersive X-ray analysis on scanning electron microscopes (SEM), and the electron microprobe are all essentially blind to lithium

(Schowengerdt, 1985). Furthermore, mass spectrometric measurements at low mass positions are subject to serious instrumental mass discrimination effects (Chan 1987, Gregoire, 1989a) thereby making isotope ratio measurements difficult, while other techniques, such as neutron activation and atomic absorption, free from this difficulty (Brown et al., 1978; Meier 1982) lack the inherent precision required to make such measurements. Consequently, not much information exists in the literature concerning the use and applications of lithium isotope ratios in the field of earth sciences.

The Inductively Coupled Plasma Mass Spectrometer (ICP-MS) has the potential to offer a reliable method for the determination of Li isotope ratios. ICP-MS has already been applied successfully to isotope ratio measurements of the light element, boron, in geological materials (Gregoire 1990, Gregoire 1987, Takao et al., 1989), and the question is, whether the isotopic fractionation of lithium isotopes caused by natural processes is of such a magnitude to be resolved by ICP-MS. Gregoire, (1989a) states that "the extent of isotopic fractionation is related to several factors including the absolute mass of the element, and the relative mass difference between two isotopes of the same element, the chemical reactivity of the element, and the number of enrichment cycles (e.g., distillation) completed". It is the lighter elements, and those with greater relative mass differences, that will be affected the most by mass discriminating processes (Faure, 1986). With this in mind, and considering the fact that lithium is completely ionized in the argon plasma (Houk and Thompson, 1988), and is not affected by either polyatomic or isobaric interferences from other elements or from plasma species (using an Ar plasma), ICP-MS

may be considered a good candidate technique for the measurement of Li isotope ratios.

In general, however, ICP-MS has not been widely used for the determination of lithium. In fact, lithium isotope ratio measurements using this technique have enjoyed only limited success for biological samples (Sun et al., 1987; Vanhoe et al., 1991), and have not been successfully made for geological samples to date. The problem is two-fold. First, the low mass of lithium heightens its susceptibility to mass discrimination (i.e., the unequal transmission of ions through the interface, ion lenses and mass spectrometer on the basis of mass) in the ICP-MS instrument (Gregoire, 1990). Fortunately, instrumental mass discrimination may be corrected for. Second, and more daunting however, is the problem of instrumental contamination by high levels of lithium. ICP-MS instruments are costly, and most laboratories are not provided the luxury of having an instrument dedicated solely to lithium isotope studies. As a result, the majority of instruments will likely be employed a great deal of the time performing routine analysis (i.e., other than Li analysis) of various samples. These samples are frequently decomposed using a lithium metaborate flux, and as a result, very high lithium salt concentrations are continuously being passed through the ICP-MS causing a high level of lithium contamination throughout the instrument. Some workers have reported that the measurement of lithium isotope ratios by ICP-MS is "impossible" since the lithium signal is dominated by contamination (Russ and Bazan, 1987). Perhaps as a result of this, the majority of measurements to date of lithium isotopic composition have been made using Thermal Ionization Mass Spectrometry (TIMS).

Early measurements of lithium isotope ratios have been summarized by Heier and Billings (1970), and De Bievre et al. (1984). The majority of the measurements compiled by these authors were performed using thermal ionization mass spectrometry (TIMS) of lithium in a variety of forms: for example, LiCl (Taylor and Urey, 1938; Lamberty et al., 1992), LiI (Michiels and De Bievre, 1983; Flesch et al., 1973), and most recently, lithium metaborate (Chan 1987, Chan and Edmond, 1988). Sample preparation procedures for TIMS protocols generally involve separation of lithium from its matrix followed by a conversion of the lithium to a molecular form for analysis. Reported methods include, precipitation from solution as perchlorate and conversion to the sulphate form for analysis (Wanless et al., 1970), separation by ion exchange in a two column technique (with recorded lithium recoveries of as low as 50 %) followed by direct analysis (Balsiger et al., 1968), and cation exchange separation followed by a two-step conversion to $\text{Li}_2\text{B}_4\text{O}_7$ (Chan 1987) to name a few.

After thermal ionization mass spectrometry, the second most popular technique employed has been neutron activation analysis. Neutron activation of lithium extracted from stone meteorites, via ion exchange and converted to the chlorate form, was performed by Brown et al., 1978 and Rajan et al., 1980. In addition, lithium isotope measurements have also been attempted using atomic absorption spectrometry (Meier, 1982), and the ion microprobe (Wu and Tong, 1991; Cunningham et al., 1983; and Lowry et al., 1981). Neither neutron activation (Murty et al., 1982, Rajan et al., 1980), nor atomic absorption spectroscopy (Meier, 1982), nor ion microprobe techniques are suitable

methods for the determination of lithium isotope ratios. None can achieve the precision required for measurement of ratios in geological materials (better than 0.2 %): neutron activation reporting a precision of 1 % (Rajan et al., 1980), atomic absorption reporting a precision of only 2-4 % (Meier, 1982), and ion microprobe techniques unable to improve on 1 % precision (Wu and Tong, 1991).

The use of ICP-MS as a method for lithium isotope ratio determination has been reported only twice in the literature (Sun et al., 1987, and Vanhoe et al., 1991). Both of these authors were interested in the lithium isotopic composition of biological materials. One approach used ^9Be as an internal standard (Vanhoe et al., 1991) with poor precision (approximately 3 %), and no correction for mass discrimination. The other (Sun et al., 1987) used external calibration of the instrument with solutions of known isotopic composition mixed from two enriched isotopic standards (i.e., ^6Li enriched and ^7Li enriched materials) prior to measurement. The precision obtained by this method was approximately 1 %.

The principal errors in neutron activation techniques involve errors contributed from interfering reactions, errors resulting from target thickness, and errors resulting from pulse pile-up (Brown et al., 1978). In atomic absorption spectrometry, the principal absorption lines for ^6Li and ^7Li are very close together, and when coupled with the factors that result in peak broadening, result in some degree of spectral overlap. This method at best can be used only as a means of estimating the Li isotope composition (Greenwood

and Earnshaw, 1984). Finally, ion microprobe analysis is subject to contamination from inclusions, and does not possess the precision required to resolve differences in isotopic composition as a result of natural isotopic fractionation processes (Wu and Tong, 1991).

TIMS on the other hand, is a precise and accurate method for measuring lithium isotope ratios. The main drawbacks with thermal ionization mass spectrometry arise from the need to use very small sample sizes (as low as 1 μL ; Michiels and De Bièvre, 1983) and the need to convert Li into other forms prior to analysis. Most TIMS procedures involve rather long and complicated sample preparation steps in order to form molecular ions. Both excessive sample handling, and the use of small sample aliquots for measurement, add potential sources of error to the method. In addition to this, the long sample measurement time (2-6 hours per sample) make measurements by this method tedious and expensive.

ICP-MS offers the advantages to isotopic measurements of: (1) long-term steady-state signals (provided by sample solution nebulization into the plasma) permitting the achievement of the counting statistics needed for high-precision measurements, (2) low detection limits for lithium, allowing a relatively small amount of sample to be nebulized for a comparatively long period of time, and (3) freedom from spectral interferences at the lithium ion mass spectral peaks (this may or may not be the case for molecular ions measured by TIMS). In addition, samples may be presented in aqueous solution, thereby simplifying sample preparation and reducing resultant errors.

The purpose of the work described in this thesis was to develop an ICP-mass spectrometric technique suitable for precise determination of the lithium isotopic composition of geological materials, and thereby, conduct a reconnaissance study of lithium isotope ratios in various minerals to search for trends that might result from lithium isotope fractionation. In spite of the ability of TIMS to measure lithium isotope ratios with sufficient precision, the isotope geochemistry of lithium has not been well characterized. This study, therefore, has attempted to supplement the small pool of data presently available on the subject.

In the course of this study, lithium isotope ratios were determined for a number of sets of mineral separates:

- a) minerals of varying crystal structures to identify the general range of lithium isotope ratios observed in Li-bearing minerals,
- b) a suite of spodumene samples to define variations in bulk composition with respect to lithium isotopic composition,
- c) a suite of mica separates from a suite of previously studied topaz rholites, to compare lithium isotope ratios of each mica sample to the oxygen and hydrogen isotopic composition of the whole rock samples.

Samples for this study were acquired from various sources. The majority of the spodumene samples were supplied by F.W. Breaks, the mica suite and one spodumene sample was supplied by R.P. Taylor, the hectorite was supplied by Joan Carles Melgarejo, the griceite was supplied by J. W. Van Velthuisen, and the remainder of the samples were

supplied by the Canadian Museum of Nature.

Part I of this work deals with the development of the ICP-MS technique for the measurement of lithium isotope ratios, including sample preparation methods, and the measurements of reference standards. Part II of this work presents the determinations made on the above-mentioned suites of samples, and identifies observable trends in isotopic compositions. It is hoped that the presentation of this method and these data may fuel renewed interest in Li isotope geochemistry and perhaps enable further studies to be done. The specific objectives of this research were as follows:

1. to optimize ICP-MS conditions so that the precision of Li-isotope ratio measurements was better than 0.3 %, the precision required to detect the small shifts in isotope ratios of minerals resulting from geological processes;
2. to develop a technique of sample dissolution for geological samples to be studied using ICP-MS which did not result in any procedural isotope fractionations or lithium contamination;
3. to select and optimize a separation technique for lithium that is quantitative, and compatible with ICP-MS direct measurement;
4. to perform Li-isotope measurements using the developed procedures;
5. to analyze collected ratio data from various mineral suites, and
6. to identify any natural variations in lithium isotope ratios that may be related to fractionation and to describe these variations.

CHAPTER 2

DEVELOPMENT OF INSTRUMENTAL PROTOCOL FOR LITHIUM ISOTOPE MEASUREMENTS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

2.1 INTRODUCTION

The feasibility of an ICP-MS stable isotope study of a particular element is strongly dependent on a number of innate factors of the isotope system in question, as well as to the manner in which each isotope behaves in, and is affected by the plasma. The isotope system must, of course, have at least two stable isotopes, each of which is not involved in the radioactive decay sequence of another element (Faure, 1990). The relative mass difference between the two isotopes must be large enough to allow measurable fractionation by natural processes to occur. Isotope fractionation occurs as a result of "the isotope effect" [i.e., the differing physicochemical behaviour of isotopes of the same element solely dependent on differences in their nuclidic masses (Karplus and Porter, 1970)]. Ideally, the elemental masses of each isotope should be free from isobaric influences [i.e., the isotope of a different element with the same atomic number, Z , (Faure, 1990)], and plasma generated isobars (i.e., elemental ions with the same mass/ Z as the element in question). Finally, an ideal situation finds the two isotopes present in sufficient relative quantities to one another, that having the less abundant isotope present in solution

at a concentration within the detection limit of the ICP-MS (0.01 ppb), (Elan 5000 Users' Manual), does not force the more abundant isotope out of the linear response range of the detector (the ELAN is linear to approximately 500,000 ion counts per second; D.C. Gregoire, personal communication, 1994). Lithium has only two isotopes (mass 6 and mass 7), both of which are stable, and which have a relative mass difference of 15 % [this is large for isotope systems (Faure, 1990)]. Neither ^6Li , nor ^7Li is created through the radioactive decay of another element, and no elemental isobars are present at these masses (Faure, 1990). No ionic isobaric interferences (i.e., ion with same mass/Z as Li) are created in the argon plasma (Horlick et al., 1987; Gray, 1988). Finally, the relative abundances of the two isotopes (7.5 and 92.5 wt % for ^6Li and ^7Li respectively; Horlick et al., 1987) are such that both of the isotopes, when present in natural abundances, are within the linear detector response range of the ELAN 5000 ICP-MS.

ICP-MS measurements are inherently prone to certain types of interferences that can adversely affect the measurement of an isotope ratio. They include: mass spectral overlap due to plasma-induced polyatomic ions, matrix-induced polyatomic ions (e.g., oxide ions), and matrix-solvent-induced polyatomic ions (i.e., due to the use of acids in the plasma), or doubly charged ions; ionization suppression by other plasma ions; and instrumental mass discrimination, particularly against low mass ions (Douglas and Houk, 1985; Date, 1985; Date and Gray, 1985). Lithium is not subject to any mass spectral interferences in an Ar plasma, with an inorganic matrix (Gregoire, 1989a), and fortunately, lithium has one of the lowest ionization potentials (5.39eV), making it essentially immune

to ionization suppression by other ions. It has a predicted ionization efficiency of >99.85 % in a 6680 K plasma (Horlick et al., 1987), and a 100 % predicted efficiency in a 7500 K plasma (Fiouk and Thompson, 1988), and has a very high second ionization potential (Cotton and Wilkinson, 1980), which prevents the prevalence of a Li^{2+} population in the plasma.

Two of the limitations of ICP-MS in lithium isotope studies are; the instrumental mass discrimination suffered by the low mass elements (Gregoire, 1989a; Horlick et al., 1987; and others), and the less easily correctable matrix-induced mass discrimination (Gregoire, 1989a). But by far the most serious limitation of applying this method to the measurement of lithium isotope ratios, is the problem of contamination. Instruments which perform routine analyses on samples digested with lithium metaborate flux, have continuous inputs of very high lithium salt contents (~10 %). Consequently, lithium contamination of the instrument is pervasive. The problem of instrumental contamination by lithium has led some workers to conclude that performing meaningful lithium isotope ratios is impossible, inasmuch as the lithium signal is dominated by contamination (Russ and Bazan, 1987).

The ultimate determination of the success or failure of ICP-MS as a satisfactory method for lithium isotopic studies, depends upon the precision of the ICP-MS ratio measurement being sufficient to detect variations in the isotopic composition of minerals caused by natural processes (<0.3 %). In order for this to be possible, it is necessary to

overcome the problems of mass discrimination (both instrumental and matrix-induced), and most importantly to overcome the difficulty of instrument contamination. Furthermore, it is also necessary to minimize the effect of instrumental instabilities (both short term and long term) on the precision of the isotope ratio.

The following pages outline the experiments that were done and the steps that were taken to optimize the ICP-MS working conditions for the measurement of lithium isotope ratios.

2.2 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

2.2.1 - Instrumentation

All experiments were performed using the Perkin Elmer Sciex Elan Model 5000 quadrupole mass spectrometer. A quartz torch and alumina sample injector tube were used, and samples were introduced via a Rytan nebulizer spray chamber supplied with sample by a Gilson peristaltic pump delivering 1 mL per minute. Pure argon (99.9 % Ar) was used as the nebulizing, plasma, and auxiliary gas. The sampler and skimmer cones were made of nickel and dedicated solely for use with lithium isotope measurements to avoid contamination with lithium salts from other applications.

A schematic of the ELAN 5000 Inductively Coupled Plasma Quadrupole Mass Spectrometer is shown in Figure 1. The sample, in aqueous solution, is pumped into the

a)

b)

Figure 1: Schematic Diagram of a) ELAN 5000 Inductively Coupled Plasma-Mass Spectrometer and b) ELAN 5000 Ion Optics

nebulizer spray chamber assembly via a peristaltic pump, and then carried into the argon plasma via an alumina injector tube, by a flow of argon gas (nebulizer gas). An argon plasma is induced by an RF load coil with four turns around a quartz torch, and the ion stream is directed at a nickel sampler cone with a 1.1 mm orifice. Much of the argon gas is rejected at the sampler cone, and the remaining ion beam passes through the sampler/skimmer interface region (maintained at a pressure of 4 torr). After passing through the sampler/skimmer interface region, the beam is directed onto the skimmer cone orifice (0.89 mm), where the flow of gases is further restricted. From there, the ion beam enters the first vacuum chamber maintained at a pressure of 8×10^{-4} torr, and is focused by a series of ion lenses. The ion optics consist of the following components:

- 1) Einzel lens: The Einzel lens is a three-cylinder lens set, that focuses the broadened ion beam from the skimmer cone into a narrower beam. E1 controls the potential on the first and third cylinders. The potential at E2 is constant (Figure 1).
 - 2) Bessel box: The ion beam is then directed into a lens set called a Bessel box. The large cylinder forming the perimeter of the box is the B lens.
 - 3) Photon Stop: The ion beam travelling into the Bessel box is diverted in a curved path around a small disk called a photon stop (S2 lens), located directly in the ion path. The function of the photon stop is to form a barrier to unwanted photons from the ICP. Charged ions may curve around the photon stop while photons cannot.
- Once they have passed through the ion optics, the focused ions are directed into the quadrupole mass spectrometer. The quadrupole mass spectrometer acts as a mass filter.

It is constructed of four parallel metal rods, which can selectively allow ions having a given mass/charge ratio to pass through at any moment in time. All other ions collide with the rods, exit out of the path between the rods and are dumped out of the system. The ions with the desired energy are then directed onto the channel electron multiplier (CEM) detector.

2.2.2 - Reagents/Labware

All experiments in this section were performed with a 100 ppb Li solution diluted from a commercial 1000 ppm spectroscopic lithium standard (SPEX Spectroscopic Lithium Standard, Specpure Industries Inc., Edeson, N.J.), in ultrapure, de-ionized water with a resistivity of 18 M Ω obtained from a Milli Q2 water purification system (Millipore Corp., Mississauga, Ontario). Argon used in the ICP operation was >99.9 % pure.

2.3 OPTIMIZING ICP-MS OPERATING CONDITIONS

The following section outlines the experiments performed in optimizing ICP-MS operating conditions for the measurement of Li -isotope ratios. The instrumental operating conditions were optimized with three criteria in mind: 1) maximizing Li sensitivity, 2) maximizing Li signal stability, and 3) minimizing the contribution to the lithium signal from background lithium contamination (dominated by instrument contamination). The last two of these criteria are the most crucial since, as has already been noted, a high degree of precision (>0.3 %) for ratio measurements will be required if

the method is to satisfy the requirements of any geological application. A final consideration where the measurement of isotope ratios is concerned, is the examination of the sources of mass discrimination during sample measurement, with a view to strategies for correcting for mass bias.

2.3.1 - Definitions

- Auxiliary Gas:** the auxiliary gas flow is the argon flow that interjects between the outer plasma gas flow and the central nebulizer gas flow (which carries the analyte). Its purpose is to push the plasma away from the central and middle tubes, thereby preventing melting.
- Background:** the background is defined as the lithium signal obtained when no sample solution is being aspirated.
- Blank:** the blank is defined as the lithium signal obtained when a sample matrix solution with no analyte present, is aspirated into the plasma. The blank combines contributions from the background and the matrix solvent, to the lithium signal.
- ICP:** the Inductively Coupled Plasma (ICP) is formed by coupling radio frequency (RF) power into flowing argon. This creates a plasma with a temperature ranging from 6000 K to 8000 K. The plasma is formed within an ICP torch, which is a series of three concentric quartz tubes, through which argon flows at different rates.
- Intensity:** intensity is defined as the total intensity (in counts per second) of

	the isotope being measured
Intensity RSD:	this is the relative standard deviation (RSD) for the particular isotope as a percentage, after a number of replicate measurements.
Nebulizer Gas:	the nebulizer gas flow is the central argon flow which carries the analyte and directs the sample aerosol through the center of the plasma.
Net Intensity:	the net intensity is defined as the intensity (cps) of the isotope minus the intensity of the blank.
Plasma Gas:	the plasma gas is the argon flow that is closest to the RF load coils. It flows between the outer and middle tubes of the ICP torch, and it is this gas flow that is coupled to the load coil by electrical inductance to form the plasma jet. In addition to sustaining the plasma, it also cools the outer quartz tube to prevent melting.
Plasma Power:	the plasma power setting indicates the radio frequency (RF) power (in watts) that is coupled with the flowing argon to create the plasma.
Sensitivity:	sensitivity is defined as the number of ion counts per second (cps) of a given element for a 1 ppm solution (Elan Users Manual).

2.3.2 - Plasma Power, Auxiliary Gas Flow Rate, Plasma Gas Flow Rate

Plasma Power

Figure 2 shows the change in sensitivity for the $^7\text{Li}^+$ ion as a function of plasma

power. Measurements for this experiment were made on a 100 ppb Li solution and total count rates (average of 5 consecutive measurements) were recorded at each power setting (their normalized values being plotted on the graph). No data points were collected for background lithium values. It can be seen from Figure 2 that sensitivity for ^7Li increases continuously with increasing plasma power. However, it is likely that the ^7Li background signal is also increasing with plasma power, as the increased plasma temperature results in more desorption of contaminant lithium from sites within the instrument, although no data has been collected to confirm this. Below 800 watts, the plasma becomes increasingly unstable (i.e., RSD of five consecutive measurements at points below 800 watts are >2.5 times higher than RSDs for $n=5$ measurements for points between 800-1150 watts).

The overriding criterion for the selection of the RF power level for measurement, is the background contribution to the ^7Li signal. In the interest of minimizing the population of desorbed background lithium in the mass spectrometer, yet maintaining a high sensitivity for ^7Li , a plasma power of 1000 watts was selected for the measurement protocol.

Plasma Gas Flow Rate and Auxiliary Gas Flow Rate

Figure 3 depicts the relationships between the various gas flow rates and the ^7Li sensitivity. Five replicate measurements of a 100 ppb Li solution were made at each flow rate, and the normalized values were plotted on the graphs. Observations were made of the effect of these two gas flow rates on the background signal for lithium. Neither gas

Figure 2: The effect of plasma power on ^7Li ion intensity.

Figure 3: The effect of gas flow rates on ^7Li ion intensity: (a) nebulizer gas flow varied; (b) auxiliary gas flow varied; (c) plasma gas flow varied.

flow had any significant effect on the background level. Neither the plasma gas flow rate and the auxiliary gas flow rate had a large effect on the ^7Li signal, therefore the manufacturer recommended settings of 15.0 L/min for the plasma gas flow rate and 0.8 L/min for the auxiliary gas flow rate were selected for the measurement protocol.

2.3.3 - Nebulizer Gas

The nebulizer gas flow rate exerts a strong influence on lithium ion sensitivity (Figure 3), background signal (Figure 4), and mass discrimination (see Figure 12, section 2.6.1). The nebulizer mass flow controller used with the ELAN 5000 is designed to maintain stability in flow rates, up to 1.1 L/min (D.C. Gregoire, personal communication, 1994). Figure 3a illustrates the relationship of the nebulizer gas flow rate to the normalized net ^7Li intensity at flow rates up to this level, and Figure 4 reflects the effect of varying the nebulizer gas flow rate on the intensity of the background ^7Li signal. Experiments were performed using a 100 ppb Li solution, and blank values were subtracted at each flow rate plotted on Figure 3a.

A very strong dependence on nebulizer gas flow, for both background signal and analyte signal, is demonstrated in Figures 3a and 4. At nebulizer gas flow rates of 0.7 L/min, both the analyte signal and the background signal have the same intensity and isotope ratio (see Figure 12, section 2.6.1). As the flow rate is increased, the net ^7Li signal reaches a maximum (at 1L/min in Figure 3a), and then declines, while the background signal decreases continually with increasing gas flow. From Figure 7 (section

2.4.4), we can also see that the precision of the Li isotope ratio measurement is greatest at 1 L/min, and at flow rates above this, the ratio RSD increases.

As nebulizer gas flow is increased, the size and the temperature of the ICP vary. A higher nebulizer gas flow cools and elongates the plasma, causing the radiation zone to be extended farther towards the sampling cone (Horlick et al., 1987). The results of Figure 4 indicate that a cooler plasma discourages the desorption of contaminant lithium from surfaces within the instrument, thus decreasing the background lithium signal. From Figure 3a we may deduce that the net lithium signal is enhanced by a slightly cooler plasma, but then degraded by any further cooling. The shape of the curve observed in Figure 3a is typical of what is observed on the ELAN 5000. The absolute location of maximum sensitivity to lithium with respect to nebulizer gas flow rate, however varies from day to day, as does the absolute maximum sensitivity (in counts per second) to lithium.

Several factors may contribute to decay in lithium sensitivity. They include degradation of the sampler or skimmer orifices, scale buildup in the plasma torch, melted or misshapen quartz torch, wearing, cracking or melting of O-rings, drift in mass calibration, wear on mass flow controller, drift in ion optics, or corrosion of RF load coil (Elan User's Manual). Any or all of these factors may also affect plasma conditions (i.e., plasma temperature or shape) such that maximum lithium sensitivity is achieved at a flow rate other than 1 L/min. Because of the important influence of the nebulizer gas flow rate

Figure 4: The effect of nebulizer gas flow on ^7Li background signal

on the measurement conditions of lithium, this parameter was optimized at the beginning of each analytical session to the point of maximum analyte sensitivity. This value varied from ~.94 L/min to >1.2 L/min, and in general was between 1.0 and 1.1 L/min. In all cases however, the nebulizer gas flow rate was higher than the manufacturer recommended optimum value of 0.9 L/min.

2.3.4 - Torch Position

As we have noted in the previous section, a number of factors affect the condition of the plasma. In particular, as the nebulizer gas flow rate is increased, the initial radiation zone is pushed toward the sampling cone (Horlick et al., 1987) causing a different portion of the plasma to be sampled. It was found to be necessary, therefore to reposition the torch to achieve a better sensitivity for lithium. In fact, with a centered torch and a high nebulizer gas flow rate (>1L/min), lithium sensitivity was nearly at background levels.

For this experiment, the torch was moved in a vertical plane (Y-direction), then in a horizontal plane (X-direction) to determine the position required for the highest sensitivity to lithium. A 100 ppb Li solution was aspirated into the plasma, and the count rate was observed until a maximum value was achieved. The optimum torch position relative to the sampler orifice, is shown in Figure 5.

At the high nebulizer flow rates required for analyzing lithium (> 1 L/min), the plasma is elongated toward the sampler orifice (Horlick et al., 1987). This elongation

Figure 5: Pictured is a nickel sampler covered, near the center, in a light grey residue. The residue was deposited by the plasma during a 14 hour analytical session, and visually, represents the torch position over the sampler. The torch position optimized for lithium isotope ratio measurements, is slightly off-center with respect to the sampler's orifice (center). The actual diameter of the sampler is about 5 cm and the orifice is 1.14 mm.

causes the hottest portion of the plasma (the outermost region) (Gray, 1988), to advance, resulting in a more inward (and cooler) region of the plasma to be sampled at the sampler orifice (D.C. Gregoire, personal communication, 1994). As a result it becomes necessary to reposition the torch away from the center of the ICP, in order to sample a region of the plasma with a higher population of Li^+ ions. This annular region of the plasma apparently has a higher temperature than the central region under the conditions of high nebulizer gas flows (Gray, 1988). As with the nebulizer gas flow, this parameter had to be optimized at the beginning of each analytical session. As noted in Figure 5, the optimum position for the torch is slightly off-center with respect to the sampler orifice.

2.4 OPTIMIZING THE LITHIUM SIGNAL

2.4.1 - Sources of Instrument Contamination

The use of the ELAN for routine analysis of samples digested with lithium metaborate flux, is a major contributor to the problem of instrumental contamination. For the purpose of making lithium isotope ratio measurements, it necessary to analyze samples with lithium concentrations near 60 ppb (see Section 2.6.3). At such low analyte levels, contamination of the apparatus with detectable amounts of lithium is a severe problem. Contamination can occur anywhere from the sample introduction system, to the sample interface region, ion optics or mass spectrometer. Lithium contamination of the peristaltic pump tubing, nebulizer spray chamber, alumina injector tube, sampler and skimmer, and interface region may be easily controlled by thorough cleaning prior to each analytical

session, by wiping with 3 % v/v HNO₃, and by dedicating tubing, an injector tube and a sampler and skimmer solely for use for lithium ratio measurements.

A more serious problem, however, is contamination occurring within the instrument beyond the reach of manual cleaning. Extended rinsing, by aspirating 3 % v/v HNO₃, or by aspirating 0.2N HCl proved unsuccessful in reducing the background signal caused by contamination. Although increased nebulizer flow was successful in reducing background levels significantly, in the worst case, background levels could still be as much as nearly 10 % of the analyte signal (assuming a 60 ppb analyte concentration); in the neighbourhood of 8,000-12,000 cps. It was found that altering ion lens voltages away from the manufacturer-specified settings resulted in a dramatic decrease in the amount of desorbed lithium reaching the detector (see next section). Even so, immediately following an analytical session in which lithium-fused samples were analyzed, the detector was prone to spiking (sometimes $> 3 \times 10^6$ counts!) for up to 8 hours. For this reason, it was necessary to arrange analytical sessions such that at least 8 hours of other analyses intervened between the use of the ELAN for analyses of lithium-fused samples, and the use of the ELAN for the measurement of lithium isotope ratios.

2.4.2 - Ion Optics

There are four ion lens settings that may be varied on the ELAN 5000; the E1 lens, the P lens, the B lens, and the S2 lens (Figure 1). The E1 lens setting controls the potential on the first and third cylinders of the Einzel lens. The P lens setting controls

voltages to the entrance and exit plates on the Bessel Box. The B lens setting controls the voltage of to the Barrel lens, and the S2 setting controls the photon stop. The manufacturer-recommended settings for the ion lenses (first line in Table 1), were unsatisfactory for the measurement of isotope ratios, with a signal-to-blank ratio <50 for a 100 ppb lithium solution. Since analyte lithium and desorbed contaminant lithium have different sources, they should focus differently through the ion lenses (D.C. Gregoire, personal communication, 1994; Hall, 1992; Tanner, 1993). Therefore, a set of ion lens voltages was desired that would attenuate, to some degree, the background signal, without decreasing, to any significant extent, the sensitivity to analyte lithium.

Several ion lens settings were tested, and those with the highest sensitivity to lithium (i.e., $\sim 3 \times 10^6$ cps for 1 ppm) are listed in Table 1. The two criteria for lens setting selection were a high sensitivity for analyte lithium, and a low sensitivity for background (i.e., desorbed) lithium. Table 1 summarizes the results of six sets of ion lens settings that produced a good sensitivity to lithium. The manufacturer-recommended ion lens settings were tested first, and the response to lithium at these settings was recorded. Subsequent settings that gave a similar or improved sensitivity for lithium were then selected. Many combinations of ion lens settings were observed in order to select the six shown in Table 1.

There are a large number of ion lens combinations that may produce similar conditions (D.C. Gregoire, personal communication, 1992), and each instrument will likely

Table 1: Optimization of Ion Lens Settings of the ELAN 5000 ICP-MS for Lithium.

P	Lens			Analyte ¹	Background ²	Signal to Blank Ratio
	B	S2	E1	⁷ Li (cps)	⁷ Li (cps)	
50	50	50	25	264400	5697	46
47	47	45	32	274129	4043	66
40	51	44	32	300856	5680	52
40	51	34	32	282313	5538	50
45	51	56	32	294421	5764	50
59	59	40	46	290804	2367	119

¹The analyte was a 100ppb solution of SPEX spectrographic lithium standard from SPECPURE chemicals, diluted in distilled deionized water.

²The blank solution was distilled deionized water with a resistivity of 18 MΩ.

require slightly different settings. Based on these results, however, the last set of lens settings in Table 1 (viz: $P=59$, $B=59$, $S2=40$, $E1=46$) was selected for the measurement protocol of lithium isotope ratios. It was this group of settings which produced the highest signal/blank ratio ($=119$), while still retaining good sensitivity to analyte lithium. Transmission efficiency of the background signal and the analyte signal by the ion lenses differs because background lithium and analyte lithium originate from different sources. The analyte lithium is focused by the plasma onto the sampler, skimmer and into the ion lens assembly, while the background lithium desorbs from various surfaces within the instrument, and therefore has no particular focus. As a result, behaviour of the two signals as they are influenced by ion lens voltages will be dissimilar under identical ion lens conditions (see Table 1) (D.C. Gregoire, personal communication, 1994).

2.4.3 - Memory and Rinsing Time

While it may only take a short time for a sample to be detected by the ICP-MS once it is aspirated, it often takes longer for its signal to dissipate once aspiration is terminated. This effect is commonly referred to as "memory", and is primarily the result of the adhesion of tiny droplets to surfaces within the sample delivery system (i.e., sample tubing, nebulizer spray chamber, or injector tube). Rinsing between samples, therefore, must be of a sufficient duration to eliminate any of the system's "memory" of the previous sample. The duration of rinsing between samples must exceed the time required, after the cessation of sample aspiration, for ion intensities to return to background levels. In Figure 6, the sampling tube was inserted into the sample at time=0 and withdrawn at time=100 s.

Figure 6: Rinsing Time vs. Log Ions per Second. A solution of 100 ppb Li is aspirated at $t=0$, and the tubing is withdrawn at $t=100$ s. The baseline returns to normal 120 s later.

It can be seen that about 40 seconds are required (the exact time will vary with sample tubing length) for the analyte signal to reach a steady state. Approximately 120 seconds of rinsing time are required for the signal to dissipate completely (i.e., 120s from the time the tubing is withdrawn from the sample). This experiment was performed with a 100 ppb solution of lithium. Therefore, a minimum rinsing time of 2 minutes should be used between samples with concentrations below 100 ppb lithium.

2.4.4 - Baseline Noise and Measurement Stability

The ICP is a relatively "noisy" ion source; the noise spectrum containing components in the range of 0.1-10 HZ (Gray, 1988). Typical baseline "noise" levels, reflected in short-term RSD, are 1-3 % (Horlick et al., 1987). The long-term instability of the signal (i.e., drift over time) can approach 10 %. In order to perform isotope ratio measurements precise enough to be useful in geological applications, it is absolutely essential to obtain a stable signal. Long-term instrumental drift can be attributed to causes such as salt deposition on the sampler and skimmer cones, on interfaces, or on the ion lenses, electronic stability, drift in mass calibration, and gradual changes in background levels (Gregoire, 1989a, Douglas, 1985; Elan User's Manual). Short-term fluctuations may be caused by turbulence in the nebulizer spray chamber (i.e., related to nebulizer gas flow), deterioration of sample tubing (resulting in pulsing aspiration), formation of droplets on the nebulizer, plasma flicker, electronic noise, and dissolved solids in the sample solution (Gregoire, 1989, Douglas, 1985).

Figure 7 shows the effect that nebulizer gas flow rate has on measurement stability. Relative standard deviations of five replicate isotope ratio measurements made at each of three nebulizer flow rates were calculated. Maximum stability occurs at 1 L/min, which coincides with the point of maximum analyte sensitivity (Figure 3a). The precision obtained in Figure 7 is much better than the 1-3 % worst case described by Horlick et al., 1987, as a result of the optimization of the data collection parameters (Section 2.5). Data collection parameters must be optimized to avoid the influence of short term measurement instability (Gray, 1988). Figure 8 shows the effect that analyte concentration has on the stability of isotope ratio measurements. Relative standard deviations of five isotope ratio measurements were at each of four ion count rates were calculated. Precision is highest at count rates just over 100,000 cps. The analytical calibration curve (Figure 9) shows the range of linear detector response to ^7Li , which extends to >350,000 cps (~75 ppb). Sample solution concentrations were adjusted to give ~120,000cps (30-60 ppb) for the measurement protocol.

As discussed in section 2.4.1, certain steps may be taken to reduce the effect of lithium contamination on the stability of the ICP-MS signal; in particular to reduce the incidence of spiking. In addition, long term stability may be enhanced by measuring solutions both with low dissolved solids content, and with low analyte concentrations. This will prevent the build-up of salts within the instrument (Douglas, 1985) and decrease

Figure 7: The effect of nebulizer flow rate on the stability of lithium isotope ratios. Five replicate measurements were used for each relative standard deviation calculation.

Figure 8: Variation of ratio RSD with increasing ion intensity

Figure 9: Analytical calibration curve for ^7Li .

the rate of adsorption of lithium from the sample onto instrument surfaces over time.

Long term instability cannot be eliminated however, therefore it is necessary to measure a blank and calibrate the instrument with a reference standard both before *and* after each block of analyte measurements, to correct for drift.

2.4.5 - Lithium Spectra

Once instrument operating parameters had been optimized, lithium spectra were collected under the protocol conditions to observe the peak shape and reproducibility. Figure 10 shows the superimposed lithium spectra for 20 replicate measurements of the same solution under the optimized instrument operating parameters. The peak shape is narrow and symmetrical and very reproducible.

2.5 OPTIMIZING DATA COLLECTION PARAMETERS

There are seven data collection parameters, six of which are independent. They are:

- 1) number of points per spectral peak,
- 2) number of readings per replicate,
- 3) number of sweeps per reading,
- 4) dwell time,
- 5) replicate time,
- 6) time factor, and

Figure 10: Twenty replicate measurements of the spectra of a 100ppb lithium solution using the instrumental conditions given in Table 6.

7) number of replicates.

Their relationship to each other is shown in equation (1) and (2), and their definitions are given in the following section.

(1) replicate time = (dwell time) x (time factor) x (sweeps/reading) x (readings/replicate) x (points/peak)

(2) total time (estimated) = (replicate time) x (number of replicates)

Theoretically, isotope ratios can be completed with very high precision, typically around 0.1 % RSD when acquisition parameters are properly set (Elan User's Manual). For this reason, the following section is devoted to the optimization of these acquisition parameters. A summary of the parameters selected for the measurement protocol of lithium isotope ratios is given in Table 6 at the end of the chapter.

2.5.1 - Definitions

Dwell Time: the dwell time determines the time spent measuring each specified mass (isotope) during one sweep. The same dwell time applies to all isotopes being measured.

Measurement: a measurement is defined as the average of all the replicate analyses requested for a single sample (equation 2).

Peak Hop Scanning: for steady-state analyses, the peak hop scanning mode is used.

During peak hop scanning, the mass spectrometer analyses only the

spectral peaks of the specified isotopes and omits analyzing any intermediate spectral information.

Points/Spectral Peak: the number of points per peak refers to the number of data points collected at each spectral mass during one sweep. If more than one data point is specified, they are spaced symmetrically about the spectral peak.

Readings/replicate: the specified number of readings per replicate defines how many individual readings will be taken during the course a single steady state signal analysis. If more than one reading per replicate is selected, the scanning mode is automatically set to Peak Hop Transient mode.

Replicate: a replicate is defined as the number of times the entire measurement protocol (as defined in equation 1) will be repeated for a single sample. A replicate is counted each time the defined number of sweeps are completed.

Replicate time: the replicate time determines the total time spent on each mass, for each isotope, during one replicate.

Resolution:	the peak width at 10 % of maximum peak height, defines the resolution. High resolution provides an nominal peak width at 10 % peak height of 0.4-0.6 amu.
Ratio:	the ratio is the average ratio for all replicates.
Ratio RSD	the RSD of the relative standard deviation of the ratio as a percentage.
Sweep:	a sweep is defined as one pass through the specified mass spectrum.
Sweeps/Reading:	the number of sweeps per reading determines the number of sweeps through the mass spectrum that will be averaged to yield each data point (reading). A sweep is counted each time the mass spectrometer scans from the lowest to the highest mass specified.
Time Factor :	the dwell time setting is multiplied by this value to increase the length of the time the mass spectrometer holds at the mass setting for analysis of a particular isotope.
Total Time:	the total time represents an estimate of the total measurement time for each measurement (i.e., each sample).

2.5.2 - Counting Statistics

Perhaps the most important figures of merit in stable isotope studies are the accuracy and precision of the measurement. This is particularly true of geological applications, since isotope variations occur over a limited range. The two major components which influence these figures are : (1) counting statistics, and (2) variable or unstable signal (Gregoire, 1989).

Counting statistics essentially reflect the fact that when performing analyses on a steady-state signal, the longer time spent counting each isotope, the more precise the resulting measurement will be. In essence, the short term precision possible in ICP-MS, is limited by counting statistics (Douglas, 1989), and by the noise in the ICP itself (Section 2.4.4). In counting experiments, the RSD (precision) of a Poisson distribution is given by Equation 3 (Barford, 1985):

$$(3) \quad RSD = \frac{\sqrt{n}}{n} \times 10^2$$

where, in our experiment, n would be the total number of ion counts for a given isotope during one measurement. The counting statistics described by Equation 3 require that a minimum of 10^6 counts be accumulated for the least abundant isotope during each measurement in order to attain a precision of 0.1 %.

Judiciously selected data collection parameters can make an important contribution

to optimizing the precision of the measurement of $^7\text{Li}/^6\text{Li}$ ratios. The total measurement time and time factor parameters are particularly important, as they affect counting statistics (Elan User's Manual), while the dwell time parameter is most important in dealing with the effects of short-term instrument instability (Gray, 1988). Data collection parameters must be selected in order to minimize error resulting from both of these sources. Under ideal conditions (where ICP instability is insignificant), ratio measurements would be limited only by the counting statistics (Gray, 1988).

2.5.3 - Parameter Selection

Isotopes were measured in the Peak Hop spectral scanning mode in high resolution, and peak heights were averaged during data processing. In addition, no dead time correction was applied. Dead time correction only becomes important when count rates are high, and detector response is slowed as a result (Elan User's Manual).

Points per Spectral Peak

For a steady state signal such as that obtained during solution nebulization, only one point per peak should, theoretically, be necessary (Elan User's Manual). One, two, three and five points per peak were compared (total measurement time held constant) for their respective effect on measurement stability. No significant deterioration in the ratio RSD was observed when the number of points per peak was increased from one to two. However, at three or more points per peak ratio RSD's increased more than two-fold. One point per spectral peak was selected for the measurement protocol.

Readings per Replicate, Replicate Time

The default setting for the number of readings per replicate in the Peak Hop spectral scanning mode is one. If more than one reading per replicate is selected, Peak Hop Transient spectral scanning mode is automatically selected. Only one reading per replicate was selected for the measurement protocol.

Replicate time is not an independent variable (see Equation 1).

Sweeps/Reading, Dwell Time

Since the noise components of the ICP-MS source contains components in the range of 0.1-10 Hz, it is necessary to either scan at a higher rate than this, or use relatively long dwell times on each peak to avoid this influence on the precision of ratio measurements (Gray, 1988). Table 2 shows the effects of varying dwell times on the stability of the lithium isotope ratio measurement. The other experimental conditions were:

Analyte Solution:	75 ppb Li (SPEX spectroscopic standard)
Total measurement time:	2 minutes
Number of replicates:	1
Points per Peak:	1
Reading per Replicate:	1
Time Factor for ^6Li :	7

Table 2: The Effect of Varying Dwell Times on the Stability of Lithium Ratio Measurements.

Sweeps per Reading	Dwell Time on ^7Li Peak (ms) ¹	Ratio RSD (%) ²
2	7500	2.63
20	750	0.84
200	75	0.18
2000	8	0.38

¹Dwell times for ^6Li were seven times longer than those listed for ^7Li (i.e. time factor=7 for ^6Li).

²Relative Standard Deviation (RSD) was calculated on sets of three replicate measurements.

Table 2 shows a minimum ratio RSD when the dwell time is near 75 ms (this corresponds to a dwell time of 525 ms for ^6Li because of the time factor), and the number of sweeps per reading are 200. While, a longer dwell time measures the analyte isotope more precisely, a shorter dwell time captures a "snapshot" in time, of the sample spectrum more accurately (Gray, 1988). The fact that a relatively long dwell time for ^6Li ($\sim 0.5\text{s}$) is required for maximum precision, is indicative of ICP "noise" predominantly limiting the measurement precision (Gray, 1988). A dwell time of 80 ms was selected for the measurement protocol.

Time Factor

To increase the dwell time of a single isotope, the time factor setting must be adjusted for that particular mass. To improve the counting statistics (Equation 3), counting time of the least abundant isotope (^6Li) must be long enough to ensure a minimum of 10^6 counts per measurement. The counting statistics of the ^6Li isotope are the limiting factor on the precision of the measurement, and therefore, its counting time must be increased to compensate for the lower ion count rate (Hall, 1992; Gray, 1988). Figure 11 describes the relationship between the ratio RSD and time factors for the ^6Li isotope. The experiments were performed with a 75 ppb lithium solution (SPEX, Specpure Chemicals Inc.), with a dwell time of 75 ms and 200 sweeps per reading. The remainder of the experimental conditions are the same as those for the experiment shown in Table 2. A minimum RSD is observed in Figure 11 near time factors 5 and 6. A time factor of 6 was selected for the measurement protocol.

Figure 11: Variation of ratio RSD with increasing "time factor" for ^6Li .

**Table 3: The Effect on the Stability of Lithium Ratio Measurements of
Varying the Total Time Spent on Each Measurement.**

Ratio RSD (%) ¹	Total Measurement Time (s)
.69	60
.31	120
.40	300
.43	600

¹RSD calculated on three replicate measurements.

Number of Replicates, Total Measurement Time

In the experiment summarized in Table 3, the objective was to determine the extent that total measurement time (all other factors remaining the same) affected the measurement precision. Data from Table 3 were compiled from measurements made on a 100 ppb Li SPEX solution; dwell time ^7Li =10 ms, 1 point per peak, time factor = 7 for ^6Li and 250 sweeps per reading. The total measurement time was increased by increasing the number of replicates per measurement (3, 6, 15, and 30 respectively). Relative standard deviations were calculated on groups of three isotope ratios for each measurement time. Measurement times equal to, or greater than two minutes are favoured for more reproducible results. A total measurement time ~200 seconds was selected for the measurement protocol.

The most appropriate dwell times, time factors and total measurement times have already been selected based on experiments summarized in Table 2, Table 3, and Figure 11. For these factors to remain invariant, the product between the number of replicates and the number of sweeps per reading must remain constant (Equation 1). Selecting multiple replicates causes statistical information to be automatically calculated, based on the variance between the values of individual replicates (Elan User's Manual). Therefore, using more replicates for an isotope ratio analysis provides a more meaningful statistical indication of precision for an individual measurement. The number of sweeps per reading

was reduced to 10, and the number of replicates per reading was increased to 35 for the measurement protocol.

2.5.4 - Precision of Lithium Isotope Ratio Measurements

The counting statistics for the parameter set selected for the lithium isotope ratio measurement protocol (summarized in Table 6) are calculated to give 0.07 % precision for ^6Li and 0.06 % for ^7Li , which combine to give 0.09 % for a lithium isotope ratio. However, signal instability limited the relative standard deviation for a single measurement to between 0.3 % and 0.7 %. In order to increase the precision further, isotope ratios of a sample were collected in blocks of five measurements. Net isotope ratios for each block were obtained by averaging, and the best estimate of precision (Barford, 1985) for the block of 5 measurements is given by:

$$(4) \quad \text{Best Estimate of Precision}^1 = \frac{STDS}{\sqrt{5}}$$

where, STDS is the sample standard deviation (formula in Appendix I)

¹Best Estimate of Precision is also known as the Standard Error of the Mean (Mendenhall, 1987). In this case, the mean of 5 measurements.

The best estimate of precision for a single block of measurements (i.e., one replicate determination) is generally between 0.15 % and 0.35 %. Part of this variation

within the block of measurements is due to the harmonic-like properties of the signal noise (i.e., affects the calculated RSD of a group of measurements, but does not affect the average), and the method can achieve much better precision between replicates than indicated by this value. For example, six values in Table 4 represent six replicate measurements (blocks) for a single sample (with varying amounts of Na added to the matrix). The values are: 12.316, 12.317, 12.318, 12.311, 12.315, and 12.322. The standard deviation of this group is 0.03 %. Precision between replicates of a sample is not always this high, but is certainly much improved over the standard error of a block of measurements. To assess the *representative* precision *obtainable* between replicates with the measurement protocol, 70 replicate measurements were made on 27 solutions.

Replicates types included:

- (a) blind replicates put through the entire sample preparation and analyses procedure,
- (b) sample aliquots split and put through the entire procedure separately,
- (c) sample aliquots split after dissolution, and put through ion exchange and analyses separately,
- (d) samples remeasured during different analytical sessions, and
- (e) samples remeasured consecutively.

For each block of measurements, an average isotope ratio was reported (called one replicate). From two to six replicates were measured for each of the samples, and a mean and a relative standard deviation were calculated from all replicates for an individual sample.

A *weighted* mean RSD for all samples was calculated, using the number of replicates made for each sample as the weight so that,

$$(5) \quad \frac{\sum [RSD_{(sample)} \times \text{number of replicates}_{(sample)}]}{\sum \text{replicates}} = \text{Weighted Mean RSD}$$

where, $RSD_{(sample)}$ is the RSD calculated for all the replicates of one sample, and number of replicates $_{(sample)}$ is the number of replicates that were used to calculate the RSD.

This weighted mean RSD is more indicative of the true precision of the method, inasmuch as it is not affected by the noisiness of the instrument signal. The value (from Equation 5) was calculated to be 0.08 % based on a total of 70 replicate determinations of 27 different samples. Therefore, it is more accurate to report the reproducibility of a single replicate isotope ratio determined by this method as: $X \pm 0.08 \%$, than it is to report the standard deviation or standard error of the block of five measurements. Reproducibility, as described by the weighted mean RSD, is very close to the calculated counting statistics (above).

2.6 MATRIX EFFECTS/MASS DISCRIMINATION

Measurement of isotope ratios by ICP-MS is subject to mass discrimination effects arising from; (a) instrumental conditions, (b) matrix solution composition (Gregoire, 1990), and (c) analyte concentration. "Mass discrimination is effectively, the unequal

transmission of ions of differing masses through the interface, ion lenses and mass spectrometer system to the detector" (Gregoire, 1990). Certain mass discrimination effects observed to influence lithium isotope ratios may be explained by the space charge theory (Tanner, 1992). Space charge is, in effect the broadening of the ion beam as a result of inter-ionic reactions within the beam (Tanner, 1992). The effect of this is to introduce an ion-energy induced mass bias. The effect is greatest from high mass elements onto low mass elements, and it is supposed that Ar^+ is the dominant ion exerting space charge on lithium (Tanner 1992).

2.6.1 - Instrumental Mass Discrimination

Mass discrimination resulting from instrumental conditions is caused by such things as ion lens voltages (Gregoire, 1990), and nebulizer gas flow rates (Tanner, 1993). Figure 12 shows the effect of the nebulizer gas flow on the degree of mass fractionation against both analyte and background lithium. The experiment was performed on a 100 ppb Li solution (SPEX), using the measurement protocol summarized in Table 6 and Table 7, with five ratio measurements at each flow rate. Only the nebulizer gas flow rate was varied. For both analyte and background signal, mass bias is a minimum at higher nebulizer flows.

At higher nebulizer flows, Ar^+ is less dominant as a plasma ion, and the resultant space charge effects exerted by this ion on lithium are proportionately reduced (Tanner, 1992, 1993). The effect this has on the analyte signal is observed as a decrease in isotope

Figure 12: The effect of nebulizer flow rate on the apparent $^7\text{Li}/^6\text{Li}$ isotope ratio of (a) analyte signal, (b) analyte + background signal, (c) background signal. The standard deviation of each data point ($n=5$) is within the size of the square.

ratio, as the preferential mass bias against $^6\text{Li}^+$, the lighter, and therefore, more susceptible isotope to mass discrimination, is reduced. On the background signal, the decrease in space charge, has the effect of increasing the isotope ratio. This is because at lower flows (i.e., higher space charge), the defocusing of the $^6\text{Li}^+$ ion in the plasma by space charge results in adsorption/desorption of an isotopically lighter medium onto the skimmer and sampler interfaces. Thus, the resultant background signal derived from this source is isotopically lighter at lower flow rates. As nebulizer flow increases, the defocusing is less severe, and the background signal, approaches the isotopic composition of the sample (Figure 12).

Instrumental mass discrimination cannot be completely eliminated or precisely estimated, therefore it is necessary to correct for this type of discrimination during the course of sample measurement. This is done by calibrating the instrument both before and after a sample measurement with a reference solution of known isotopic composition [carefully matched in both matrix components and lithium concentration (Sections 2.6.2 and 2.6.3) to the sample solution]. A correction factor (Equation 6) can then be calculated and applied to the intervening sample ratio.

$$(6) \quad C_f = \frac{\text{Actual Isotope Ratio}_{(\text{standard})}}{\text{Measured Isotope Ratio}_{(\text{standard})}}$$

where, C_f is the correction factor,

Actual Isotope Ratio is the Certified Isotopic Ratio of the Standard, and

Measured Isotope Ratio is the average of the ratio measured for the reference standard both before and after the sample solution.

This factor is then multiplied by the apparent (measured) sample ratio to give a corrected isotope ratio. Other types of mass discrimination (i.e., matrix-induced mass discrimination) may not be corrected for in this manner. Section 2.6.2 discusses the problem of matrix induced mass discrimination.

2.6.2 - Matrix-Induced Mass Discrimination

The 'matrix' of a sample solution is comprised of the solvent, plus any concomitant elements which occur in solution with the analyte. As with the instrumental mass discrimination effects, the lighter the atomic mass of the analyte (i.e., ^6Li), the greater its susceptibility to the mass discrimination effects of any concomitant element (Gregoire, 1989). Figure 13 displays the results of an experiment to determine the effect of various concomitant matrix elements on the mass discrimination against lithium. Net lithium isotope ratios, corrected to a reference standard, of a 600 ppb lithium solution (SPEX) spiked with varying amounts of 'matrix' elements (K, Ca, Na, Mg, Sr, and Cs), are plotted as a function of the concentration (mmol/L) of the added elements. These elements, except Cs, are typical of what may be expected in a dissolved natural mineral sample.

Na (mass 23), Mg (mass 24), K (mass 39) and Ca (mass 40) all have a mass less than or equal to the dominant plasma ion Ar^+ (mass 40). Sr (mass 88) and Cs (mass 133)

both have greater atomic masses. Na, Mg, K and Ca reduce the space charge field exerted over lithium when they supplant Ar^+ and Ar_2^+ ions in the plasma ion population. [This is a result of the magnitude of the space charge field being proportional to the mass of the space-charge ions (Tanner, 1992, 1993)]. As a result, the mass bias against the $^6\text{Li}^+$ is reduced with increasing matrix element concentration, and $^7\text{Li}/^6\text{Li}$ isotope ratios correspondingly drop (Figure 13). Similarly, addition of Sr to the matrix results in an increase in the magnitude of the space charge field experienced by lithium (mass >40), and $^7\text{Li}/^6\text{Li}$ isotope ratios progressively increase (Figure 13). The behaviour of Cs as a matrix element in Figure 13, does not fit well with this model above a Cs concentration of about 5 mmol/L. What we observe in general in Figure 13, is the higher the concentration of the matrix element, the greater its effect of the $^7\text{Li}/^6\text{Li}$ isotope ratio. Na is an exception, in that $^7\text{Li}/^6\text{Li}$ ratios stabilize at Na concentrations $\geq 20\text{mmol/L}$.

High concentrations of matrix elements clearly result in strong matrix-induced mass discrimination effects against lithium. Matrix induced mass discrimination has been observed for lithium by other workers (Gregoire, 1989a). Compensation for this effect can only be made by careful matrix matching of samples with standards, or by separation of Li from the matrix. Since mineral samples have highly variable compositions, matrix matching between sample and standard would not only be cumbersome and time-consuming, but largely imprecise. Separation of lithium from the majority of matrix elements by (a) acid-leaching of lithium from the crystal lattice, or (b) ion exchange separation of lithium, are the two approaches that will be discussed in Chapter 3. With

Figure 13: Effect of matrix element concentration on apparent $^7\text{Li}/^6\text{Li}$ ratio

**Table 4: The Effect of the Presence of Na on the Lithium
Isotope Ratio Measurement**

Concentration of Na in Sample Matrix (ppb)	Net $^7\text{Li}/^6\text{Li}$ Ratio ¹
4.8	12.316
8.2	12.317
23.8	12.318
47.8	12.311
244	12.315
488	12.322

¹Ratio measurements were performed on a 200 ppb Li solution,
with five replicates per measurement.

either of these approaches, there is likely to be a small amount of matrix elements introduced into the samples, either by co-leaching, or by incomplete resolution of ion exchange peaks. In both cases, Na in low levels will occasionally be present. Figure 13 only examines the effects of matrix elements at concentrations >50 ppm, however, the higher the molar ratio of the analyte to the concomitant element, the lower the corresponding matrix effect (Gregoire, 1990). Table 4 therefore, examines the effect of low levels of Na on the $^7\text{Li}/^6\text{Li}$ ratio.

The experiment summarized in Table 4 was performed on a 200 ppb Li standard solution (SVEC) divided into several aliquots, each spiked with different amounts of sodium. We see that no significant shift in the isotope ratio of the sample caused by concomitant Na up to 488 ppb Na (~2.5 times sample concentration of Li in ppb, or ~75 % molar ratio of Na/Li). Sun et al., 1987, found no significant isotope shift for Na/Li > 20 (in ppb) during ICP-MS measurement of Li ratios in biological samples. Not only does Table 4 reveal that Na contamination of samples (in low levels) is insignificant, but it also indicates that the presence of sodium in low levels may be beneficial to measurement stability. The calculated relative standard deviation of the six measurements on Table 4 is 0.029 %, this is nearly three times lower than the weighted, mean RSD calculated for all other ratio determinations made for this work. Perhaps future work could be directed at assessing the suitability Na as a potential "matrix modifier" for use in ICP-MS lithium isotope determinations.

2.6.3 - Concentration-Induced Mass Discrimination

Figure 9 shows the analytical calibration curve for ^7Li . Calibration of both isotopes shows linearity up to a total lithium concentration ≈ 75 ppb (i.e., ~ 71 ppb of ^7Li ; ~ 4 ppb of ^6Li). The slope of the ^6Li calibration curve is steeper however (not shown), and the result is a progressive and regular decrease in lithium isotope ratios as a function of increasing Li concentration (Figure 14). Figure 14 shows the "apparent" (i.e., uncorrected) $^7\text{Li}/^6\text{Li}$ isotope ratio as a function of lithium concentration (ppb). Perhaps this concentration-induced mass discrimination against the ^6Li isotope is analogous to the matrix-induced mass discrimination of other matrix elements below mass 40 (Section 2.6.2). In this case, $^7\text{Li}^+$ would be considered the "matrix" element responsible for the reduction of the Ar^+ -dominated space charge field exerted over the $^6\text{Li}^+$ ion, or perhaps this unusual property is just an artifact of the ELAN 5000 system. In any event, it is evident that careful concentration matching, between samples and reference standards, is crucial to obtaining a meaningful correction of lithium isotope ratio measurements, free from the effects of the concentration -induced mass discrimination.

2.7 SUMMARY AND CONCLUSIONS

Table 5 and Table 6 summarize the results of ICP-MS operating conditions, ion lens settings, and data collection parameter, optimization experiments. In addition, it should be recalled that measurement precision using the adopted measurement protocols is optimum when sample solutions are diluted to give $\sim 120,000$ ion counts per second for

Figure 14: Apparent isotope ratio as a function of lithium concentration

⁷Li. Furthermore, to ensure that short-term and mid-term instrumental instability do not affect the precision of the ratio measurement, ratio measurements are collected in blocks of 5 in the order: blank - standard - rinse - sample -rinse - standard - blank. Rinsing should be for a minimum of 2-3 minutes. The use of the reference standard (see Chapter 4 for available reference standards) to calibrate instrument response before and after ratio determinations, eliminates the influence of instrumental mass discrimination. To compensate for the influence of concentration-induced mass discrimination, careful concentration matching between samples and reference standards is required, and to eliminate the effects of matrix-induced mass discrimination, it is necessary to separate lithium from most of the sample matrix (see Chapter 3).

Possible sources of systematic error for the measurement of isotope ratios are: interface and ion lens effects (i.e., space-charge), sample introduction system (i.e., pulsating nebulisation), systematic contamination during sample preparation. Sources of random error are: random beam instability, random electronic or detector noise, sporadic desorption of contaminant lithium producing spiking, air bubbles or droplets in sample introduction system, random sample contamination during preparation (Turner, 1992).

The ultimate advantage of using ICP-MS to measure lithium isotope ratios over the more commonly used method of thermal ionization mass spectrometry, is the simpler sample preparation steps required for ICP-MS determinations (Turner, 1992).

Conclusions

1. Optimum ICP-MS operating conditions for lithium isotope ratio measurements are given in Table 5.
2. An optimum data collection parameter set is given in Table 6.
3. Background lithium contamination by lithium metaborate can be controlled by careful instrument cleaning, increased nebulizer flow rates, and optimized ion lens voltages. Analytical sessions must also be arranged so that they do not follow routine lithium metaborate-fused sample analyses by less than 8 hours of instrument time.
4. Short term instrument instability is the dominant factor in determining the precision of lithium isotope measurements by ICP-MS. However, the use of longer dwell times, time factors, total measurement times, and more replicate measurements overcome this limitation, yielding an overall obtainable precision for the method of 0.08 %. The calculated counting statistics for the suggested measurement protocol are 0.07 % for ^6Li and 0.06 % for ^7Li .
5. Mass discrimination influences lithium-lithium concentration dependent relationships in the ICP-MS, necessitating careful concentration matching of samples and standards.
6. Na exerts a negligible mass discrimination effects against either lithium isotope at concentrations of $\text{Na/Li} > 2.5$ at the ppb level.
7. Na shows promise as a potential "matrix modifier" for use in lithium isotope ratio determinations.

Table 5: Instrument Operating Parameters for $^7\text{Li}/^6\text{Li}$ Ratio Measurements

R.F. Power	1000 W
Auxiliary Gas	Ar
Auxiliary Gas Flow Rate	0.8 L/min
Plasma Gas	Ar
Plasma Gas Flow	15.00 L/min
Nebulizer Gas	Ar
Nebulizer Gas Flow ¹	1 L/min
Ion Lense Settings:	
B lens setting	59
E1 lens setting	46
P lens setting	59
S2 lens setting	40
Sampler	Nickel (orifice = 1.14mm)
Skimmer	Nickel (orifice = 0.89mm)
Sample Injector Tube	Alumina
Sample Introduction Rate ²	1 mL/min
Operating Temperature	15 °C

¹Nebulizer gas flow was optimized daily: usual value was approximately 1 L/min, but varied in the range of 0.9 to 1.1 L/min.

²Equivalent to a peristaltic pump setting of 20.

Table 6: Data Collection Parameters for $^7\text{Li}/^6\text{Li}$ Ratio Measurements

Scanning Mode:	Peak Hop
Resolution:	High
Points per peak:	1
^7Li Time Factor	1
^6Li Time Factor	6
^7Li Dwell Time	80 ms
^6Li Dwell Time	480 ms
Sweeps/Reading	10
Readings/Replicate	1
Number of Replicates	35
Sampling Time	3 minutes 16 seconds

CHAPTER 3

SAMPLE PREPARATION FOR LITHIUM ISOTOPE MEASUREMENTS

3.1 INTRODUCTION

Subsequent to defining a measurement protocol for the measurement of lithium isotope ratios (Chapter 2), it was necessary to develop a method of sample preparation for actual geological samples that would be compatible with ICP-MS. Two alternate approaches were considered for the extraction of lithium from geological samples; (1) acid-leaching, and (2) ion exchange. Because of the extreme susceptibility of lithium to matrix-induced mass discrimination effects, the Li-extraction procedure must remove most of the matrix components from the sample solution.

3.2 ACID LEACHING

Acid-leaching was the first method of Li-extraction considered as potentially suitable for Li-isotope ratio measurements. It is considerably simpler and less time consuming than complete sample dissolution followed by ion exchange separation of lithium, and has already been successfully applied in B-isotope studies (Gregoire, 1987).

Minerals samples were hand picked under a binocular microscope, crushed in an

agate mortar and pestle to 200 mesh, and ~ 30mg placed in Teflon screw cap vial with 1-2 mL each of concentrated HCl and HNO₃. The sealed vials were then heated on a hot plate at 190 °C overnight, and then evaporated at <120 °C to dryness. Approximately 5 mL of deionized water was added to the residue, and after some swirling, was decanted into a centrifuge tube. The solution was then centrifuged to remove any suspended solids, and diluted to ~50 ppb Li in deionized water.

The above procedure liberates acid-soluble Li from the crystal lattice without disrupting Si-O bonds or, presumably, other elements in tetrahedral coordination (i.e., Al). This method does not effect a complete removal of lithium from the sample, but liberates enough lithium for a satisfactory isotope ratio measurement to be performed. Further, since only Li-minerals were used as samples in this study, it was assumed that the (acid soluble Li)/(acid soluble matrix) ratio would be high enough to negate the impact of matrix-induced mass discrimination effects. Isotope ratios measured for samples prepared with this method are summarized in Table 7.

Table 7 shows a wide variation between corrected isotope ratios for each individual sample. Determinations made at different dilutions gave substantially different results for each dilution. A simple test for matrix interference is to measure the ratio for a given sample at two different dilutions. If the two dilutions give substantially different ratios, then matrix interference is the likely cause of the problem (Gregoire, 1987). This is because, when the sample is diluted, the matrix elements are also diluted and therefore,

their resultant mass discrimination effect is somewhat attenuated. The results in Table 7, therefore, indicate that matrix elements are present in acid-leached samples in sufficient amounts to cause unpredictable and uncorrectable isotope shifts. These effects can be minimized by working with extremely dilute samples, but this would degrade the precision of the ICP-MS measurements. Acid-leaching alone, is therefore, an inappropriate method of sample preparation for lithium isotope ratio measurements.

3.3 ION EXCHANGE

3.3.1 - Introduction

Based on the findings of the previous section, complete digestion of samples followed by quantitative separation of lithium from the remainder of the sample matrix is indicated for use with isotope ratio measurements. Details of the sample digestion procedure are given in Appendix III. A number of strategies may be employed to remove lithium from its concomitant matrix, including solvent extraction (Walkowiak et al, 1990a and 1990b), reverse-phased liquid ion exchange chromatography (Lee, 1993), and ion exchange chromatography with both inorganic (Abe, 1993; Bauman et al., 1993; Khan et al, 1991; Onodera et al., 1990) and organic stationary phases (Strelow et al., 1968; Johann 1989), or a combination of these. It was the objective of this part of the study to define a method of lithium separation that was i) efficient and quantitative, ii) inexpensive, iii) yielded reproducible and reliable results, and, iv) did not require the use of toxic and difficult to handle organic chemicals.

Table 7: ICP-MS Data for Samples Prepared by Acid-Leaching

Sample Number	Mineral Name	Net ⁷ Li Intensity ¹ (cps)	Net ⁶ Li Intensity ¹ (cps)	Correction Factor	Corrected Ratio ² ± Standard Error	δ ⁶ Li ± Standard Error (‰) ³
1160	Lepidolite	201,704	15,815	0.968822	12.356 ± 0.018	6.1 ± 1.5
1160	Lepidolite	175,627	13,733	0.956911	12.237 ± 0.023	5.1 ± 1.9
1160	Lepidolite	84,824	6,377	0.914614	12.165 ± 0.057	10.2 ± 4.7
HECT	Hectorite	57,501	4,211	0.896447	12.240 ± 0.071	4.1 ± 5.8
HECT	Hectorite	40,661	3,211	0.962053	12.279 ± 0.039	0.9 ± 3.2
HECT	Hectorite	39,783	3,119	0.962008	12.272 ± 0.020	1.5 ± 1.6
FB.D1	Spodumene	60,916	4,817	0.977086	12.358 ± 0.039	-5.5 ± 1.7
FB.D1	Spodumene	55,647	4,384	0.975364	12.382 ± 0.021	-7.5 ± 1.7

¹Blank has been subtracted.

²⁷Li/⁶Li ratio

³δ ⁶Li relative to the standard, IRM-016.

The most difficult elements to separate from lithium are the other alkali metals, in particular Na. The affinity series $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ is true for most exchangers (Abe, 1993), and since Na typically occurs in geological materials in greater proportions than Li, this needs to be considered in any Li-separation strategy. All separations performed in this study, were for single minerals which incorporated lithium stoichiometrically, the Na/Li proportions that needed to be separated, therefore, were much lower than would be found in a whole rock. It has already been demonstrated that Na, when present in any significant amount (i.e., ≥ 1 ppm in each sample) in the sample matrix is capable of causing matrix-induced mass discrimination in the ICP-MS, therefore the separation of Li from Na should be as complete as possible.

Johann (1989) provides a complete review of Li -separation techniques published in the literature since the 1960's. In devising a protocol for lithium separation specific to our needs, the main criteria were: a) efficient and quantitative separation of lithium from other matrix elements, b) time-efficient sample throughput, c) no necessity for organic chemicals requiring fume-hood separations, and/or with special disposal problems, d) good reproducibility, and e) relatively low cost.

The methods with the highest separation factors between Li and Na are the solvent extraction and liquid-liquid chromatography techniques (Walkowiak et al, 1990a and 1990b, Johann, 1989). These methods, however, require the use of dangerous and toxic organic chemicals that are often highly flammable and require special handling and

storage. Furthermore, their disposal is often costly and problematic. Ion exchange methods, on the other hand, generally do not require the use of organic solvents, and therefore, it was these methods that were examined in detail for this study.

Several reports of Li-selective ion exchangers have been published (Abe, 1993; Bauman et al., 1993; Khan et al., 1991; Onodera et al., 1990). Unfortunately, none of these inorganic ion exchangers are commercially available at the present time. These inorganic ion exchangers have been reported to give performance superior to organic ion exchangers for the separation of Li from Na. Inorganic ion exchangers such as λ -MNO₂ (Onodera et al., 1990), crystalline antimonite (V) acid (C-SbA) and tin antimonite acid (SnSbA)(Abe 1993), for example, have all had good success in lithium separations. The λ -MNO₂, a lithium selective adsorbent material, is prepared by an acid-treatment of a spinel type manganese oxide (LiMn₂O₄) impregnated into silica beads. Although it has extremely low distribution coefficients for other alkali metals as compared to Li (values not given by authors; Onodera et al., 1990), its reported efficiency is only 98.6 %, and it is not commercially available. Abe's C-SbA has an extremely low affinity for lithium, but a high affinity for the rest of the alkalis, causing lithium to be eluted first from the column. The separation factor for lithium and sodium on this exchanger is equal to 50. The SnSbA (Abe, 1993) inorganic ion exchanger has a high lithium selectivity, and therefore retains lithium while other elements are eluted. Lithium is then stripped from the column with a strong acid. This technique seems very promising for the selective separation of lithium from its matrix, however, this ion exchanger is also not commercially available.

Furthermore, a separation by this technique can require up to 600 mL of highly concentrated eluent (i.e., 10N HNO₃) for a 99 % recovery of lithium, and these volumes are simply not practical. Several other inorganic exchangers exist and results are summarized by Abe 1993. Most of them however, are also unsuitable. For example, the Dow Chemical company's new lithium-selective ion exchange resin (Bauman et al., 1993) is still in its experimental stages, and Khan et al., 1991 Cubic Ammonium Molybdate exchanger is about as useful for lithium separation as commercially available organic resins. The limitations of these inorganic exchangers caused them to be ruled out as potential choices for a lithium separation technique for this study.

By comparison, organic ion exchangers are well studied and documented in the literature, they are readily available commercially, and are relatively inexpensive. Furthermore, they do not require the use of dangerous organic chemicals, and they are available in highly pure form. Typically, strongly acidic cation-exchange resins are used in the separation of alkali metal ions. Organic resins most suited to the separation of the alkalis are the strongly acidic sulphonated polystyrene, crosslinked with di-vinylbenzene (DVB) (i.e., Dowex 50W-Xn and Bio-Rad AG50W-Xn, Amberlite-IR-120 (Strelow et al., 1974). However, the separation factors are small. The separation is slightly improved on the phenol-formaldehyde polycondensate resins Duolite C-3 and Bio-Rex 40. (Abe, 1993). All of these resins have a low affinity for lithium, causing it to be eluted from the column first. The separation capability of organic ion exchange resins for Li and Na are the lowest of the methods discussed so far, but this drawback is mitigated by the other

advantages of using this approach. Varying the eluent and optimizing the ion exchange conditions can have an effect on the separation factor, and thus improve the performance of this type of resin for the separation of lithium from its matrix elements for geological samples.

3.3.2 - Theoretical

As has already been mentioned, the performance of organic cation exchange resins for separating lithium may be enhanced by optimizing the parameters that affect resolution of the elution peaks. These factors include: exchange capacity of the resin, column lengths, flow rate and flow uniformity, eluent and eluent concentration. Maximum resolution for any given resin is attained when the elution peaks of respective elements are the sharpest. Betteridge and Hallam, (1972) have shown that for a 99.9 % separation of two solutes (at equal concentration), the resolution is a function of the separation factor, α , and the height equivalent of the theoretical plate (HETP). Resolution is improved by larger separation factors, or by smaller HETPs. A theoretical plate can be thought of as a single equilibrium step between the mobile and stationary phases. For systems which have relatively low separation factors (in the order of 1.6 for Li and Na on organic ion exchangers), a large number of theoretical plates is required for a good resolution (Christiansen, 1986). This can be accomplished in two ways: (1) by increasing the length of the ion exchange column, or (2) by decreasing the HETP. The van Deemter equation (Christian, 1986) defines the (HETP):

Figure 15: A graphical representation of the Van Deemter equation, showing the relative contributions of each term to the height equivalent of a theoretical plate (HETP) as a function of the mobile phase velocity (u).

$$(7) \quad HETP = A + \frac{B}{v} + Cv$$

where v is the flow rate of the mobile phase,

A represents eddy Diffusion

B represents longitudinal diffusion

C represents the mass transfer effect

A is a minimum for tightly packed columns with small particle sizes, and B and C are functions of the flow rate. A graphical representation of the Van Deemter equation is presented in Figure 15. The selection of conditions that produce the best resolution between Li and Na using organic ion exchange, is based on the relationship seen in this figure.

3.4 PROCEDURE DEVELOPMENT

The majority of techniques summarized by Johann (1989) employed organic ion exchangers; usually strongly acidic cation exchangers. A direct adaptation of one of these techniques to this study, however, would not have satisfied the criteria already stated for a separation procedure. For example, in many cases, Li was not successfully separated from Na using the recorded protocol, and in the several cases where lithium was quantitatively removed from sodium, either solvent extraction was used as a first step, multiple columns were employed, very large volumes of eluent were required, or the eluent contained a large percentage of methanol or ethanol. The procedures that utilize methanol/ ethanol, show a dramatic increase in the separation of the elution peaks for all the alkali elements,

however, the use of these solvents dictates that all separations take place in a fume hood, and that special disposal requirements be met for large quantities of waste chemicals. In addition, the quantity of high purity acid consumed per elution would cost >\$15 per sample. For these reasons, no previously published protocol was found to be particularly suitable to this study, and therefore, it was necessary to assemble a lithium separation cation exchange protocol that would meet our criteria, from the information available. By optimizing the factors which affect resolution between the Li from Na elution peaks, the satisfactory separation of Li and Na (and other concomitant elements) in mineral samples can be achieved using a single column and an organic ion exchange resin.

3.4.1 - Column and Resin

The column and resin selections were made such that a balance between maximum number of theoretical plates, optimum flow rate, and elution time was achieved. Resolution between adjacent elution peaks increases with the number of theoretical plates, and the number of theoretical plates increases with column length, and increased resin exchange capacity. In turn, resin exchange capacity is greater with smaller particle size, and a higher degree of cross-linking with DVB. However, it should be noted that the longer the column, the longer the elution times that are required. Further, the smaller the particle size, and the higher the cross-linking, the lower the flow rate that will be possible. A practical exchange procedure should take less than 8 hours, and the increase in the HETP that results from flow rates that are too slow is much greater than the resultant loss of resolution for flow rates that are too fast (see Figure 15).

Based on these considerations, a strongly acidic sulfonated cation exchange resin in the H⁺ form, Bio Rad AG50W-X8, with 8 % crosslinking with DVB (up to 16 % DVB is commercially available), and a particle size of 100-200 mesh was selected. (A smaller particle size would not have permitted gravity elution at the optimum flow rates).

Bio Rad borosilicate glass columns of 1.5 cm internal diameter, packed with 17 cm of hydrated resin were used.

3.4.2 - Eluent and Reagents

HCl was selected as the eluent for the ion exchange protocol because it, (a) has fairly good separation factors for Li and Na at low acid concentrations, (b) is available in high purity, and (c) compatible with ICP-MS and direct determinations may be made on eluted samples without further sample treatment. At lower concentrations, HCl gives better separation for Na and Li (Strelow, 1974). However, the concentration of the eluent is limited by 1) the analyte volume, which cannot exceed the volume of the sample collection bottles, and 2) the elution time, which should be kept below 8 hours. To balance the resulting volume of the collected eluate fraction, with the more efficient separation of Li from Na with decreasing HCL concentrations, samples with Na/Li ratios <2 were separated with 0.23N HCl, and samples with Na/Li >2 with 0.12 N HCl.

Contamination of the sample can occur from a variety of sources, however, any pre-column contamination that does not contain lithium is insignificant, since it will be separated by the column. Contamination during or after elution, however, is more serious,

and therefore extra steps must be taken to prevent the occurrence of this type of contamination. In order to prevent any syn- or post-column contamination, all elutions were performed using Seastar Ultrapure HCl, and column cleaning, as well as plastic cleaning steps were performed using Anala R grade HCl and HNO₃. Deionized distilled water of resistivity 18.3 megohm-cm, purified using a Milli-pore purification system, was used in all steps of sample preparation and measurement (including cleaning of plastics prior to use). And the ion exchange columns were housed in a plastic dust cabinet to prevent dust contamination.

Low Density Polyethylene (LDPE) 250 mL bottles used to collect eluent volumes, and disposable polyethylene pipette tips were cleaned prior to use with 2N HCl, followed by 2N HNO₃, and two rinses with deionized distilled water. The cleaning of these plastic resins is particularly important since Li is used in the manufacture of polyethylene (Cotton and Wilkinson, 1980). Each sample bottle and pipette tip was only used once to avoid cross-sample contamination.

3.4.3 - Flow Rate

The factors that govern the optimum flow rate are represented on Figure 15. The solvent should be eluted slowly enough that adequate time exists to establish continuous equilibrium between the stationary and mobile phases. This will result in a decreased 'tail' of the lithium peaks. The elution should not be so slow however, that diffusion processes will set in. To obtain satisfactory separations, the resin particles should be packed

uniformly in the column and the resin bed should be free from air bubbles. For most elutions a flow rate between 1.5 mL/min and 2.0 mL/min was used. Figures 16 and 17 (column calibrations) indicate that these flow rates produce good resolution of the Li and Na peaks.

3.4.4 - Column Calibration

Figure 16 shows the column calibration for 0.23N HCl and demonstrates that lithium is successfully separated from Na, K, Cs, Mg, and Sr. The column was loaded with 50 µg of Li, 32 µg Na, 4 µg K, 2 µg Cs, and 10 µg Mg, and 2 µg Sr. A slight overlap is observed between the lithium tail and the sodium peak. Another calibration was performed using only 20 µg of lithium loaded onto the column and no overlap was observed. The elution was performed at a flow rate of 2 mL/min and since it was found to be suitable to measure the collected portion of the effluent directly on the ICP-MS, samples separated by this method only required that 12.5 µg of lithium be loaded on the column (yielding a sample solution with a concentration 62.5 ppb). Due to the fact that such a small amount of lithium need be eluted, this calibration is judged to be useful for complete separation of lithium from sodium for up to Na:Li ratios of around 2.

Figure 17 show the column calibration for 0.12N HCl. To test the separation of the Na and Li peaks at this eluent concentration, 14 µg of Li and 28 µg of Na were loaded onto the column in 25mL of 0.117N HCl. The lower eluent concentration improves the separation between the Na and Li peaks over the previous calibration

Figure 16: Elution curve showing separation of lithium from other elements on Bio-Rad 50W-X8 cation exchange resin, 100-200 mesh size. 50 μ g Li, 32 μ g Na, 8 μ g K, 4 μ g Cs, and 4 μ g Mg were loaded on the column. The flow rate was 2.6 mL/min.

Figure 17: Elution curve showing separation of Li from Na on Bio-Rad AG 50W-X8 cation exchange resin, using an eluent of .12N HCl. 14ug of Li and 28ug of Na were loaded onto the column.

(Figure 16). This calibration can be used when Na:Li ratios for a sample are >2 .

3.4.5. - Column Cleaning Procedure

Figure 16 shows that Sr is still retained by the column even after 2 litres of eluent (with an increase in concentration to 0.59N HCl after 1000 mL). In addition, Crock et al., (1984) have demonstrated that on a BioRad AG50W-X8 cation exchange column, using HCl as the eluent, Ca, Sr, Ba and REE are very strongly retained on the resin, and using HNO₃ as an eluent, Fe and Zr are most strongly held. REE may not generally be present in appreciable amounts for most samples, but Ca, Fe, and Ba can be expected to occur in many geological samples.

The column cleaning procedure shown in Figure 18 was devised to strip any elements still held on the column after a sample elution, in a step-wise fashion. Figure 18 summarizes the results of a sample column cleaning. A zinnwaldite sample spiked with Ba and Sr was loaded onto the column. The first cleaning portion consists of 200 mL of 2.4N HCl followed by a water rinse (30 mL). This portion is intended to release any Na, Mg, K, Be, Ca, Zr, Ti, Al, Mn, Fe, U, V from the column (the underlined elements are those most likely to occur in an actual sample). The second cleaning portion consists of 200 mL of 2.0 N HNO₃, followed by a water rinse (30 mL). This fraction is meant to remove the remainder of Ca, Sr, Ba and REE. The elements which have been underlined are those most likely to occur in actual mineral samples. The final step is a 50 mL wash with 6N HCl that completely regenerates the resin and to removes any Sn, Zn, Ag. Not

all of these elements are shown in Figure 18, as they were not all present in the sample solution tested.

3.5 DISCUSSION, SUMMARY AND CONCLUSIONS

Recovery of lithium based on the 0.234 N calibration curve (Figure 16), where 50.0 μg of Li were initially loaded onto the column, was calculated at 50.02 μg based on lithium concentrations measured by ICP-MS. Lithium concentrations for each aliquot were measured using ICP-MS, calibrated externally with a lithium spectroscopic standard (SPEX). An aliquot of 0.23 N HCl Seastar Acid was eluted through the column, and the 200-350 mL fraction was collected and used as the blank. This lithium separation protocol, therefore, is confirmed to be quantitative.

By visual inspection of peak resolutions on Figures 16 and 17, a reasonable estimate would be that the 0.23N HCl calibration may be used when Na/Li ratios are less than about 2, and the 0.12N HCl calibration, with Na/Li ratios up to about 10. With higher sodium contents, some Na will undoubtedly be collected in the lithium fraction. This should not present a problem, provided that the total Na concentration in the collected Li fraction does not exceed more than about 2 times the lithium concentration (see Table 4). When sodium concentrations much higher than those of lithium need to be separated (i.e., whole rock samples would have Na/Li ratios 500-1000), the use of an HCl-methanol eluent might be considered. Higher eluent volumes are required for such

Figure 18: Normalized counts per second for specified elements versus total acid volume eluted through the column. A zinnwaldite sample spiked with Ba and Sr was loaded onto the column and the column was cleaned in the three stages shown across the top of the figure: a) 2N HCl (225 mL), b) 2N HNO₃ (200 mL), and c) 6N HCl (75 mL).

elutions, and all of the alcohol must be removed prior to determination via the ICP-MS, but the separation factor between Li and Na is dramatically increased over an HCl elution (Strelow, 1974).

The most convenient side-effect of this separation procedure, is that sample solutions prepared using this ion exchange protocol, may be measured directly on the ICP-MS with no further sample treatment. It is of course necessary to prepare a standard and a blank solution via ion exchange at the same time.

Conclusions

1. Acid leaching is not an appropriate method for sample preparation for lithium isotope ratio determinations by ICP-MS.
2. An acceptably high recovery of lithium is achieved by the ion exchange protocol described.
3. By using either the 0.23N HCl eluent or the 0.12N HCl eluent, samples with up to ten times more sodium than lithium may be separated.
4. Sample solutions may be measured directly on the ICP-MS with no further sample treatment.
5. The proposed column cleaning procedure in Figure 18 is effective.
6. Table 8 summarizes the ion exchange protocol to be followed prior to lithium isotope ratio measurements by ICP-MS.

Table 8: Lithium Ion Exchange Parameters

Resin	:	strongly acidic sulfonated cation
exchange resin	:	H ⁺ form
	:	8% crosslinked DVB, 100-200 mesh size
	:	(e.g. Bio Rad AG50W-X8)
Columns	:	Borosilicate glass
	:	Internal diameter 1.5 cm
	:	Packing height 17 cm.
Eluent	:	0.23N Seastar Ultrapure HCl for low Na separations (collect 100-300 mL fraction)
	:	0.12N Seastar Ultrapure HCl for high Na separations (collect 250-525 mL fraction)
Flow Rate	:	1.5 - 2.0 mL/minute
Control	:	Isotopic Reference Standard IRM-016

CHAPTER 4

METHOD CALIBRATION AND ACCURACY

4.1 INTRODUCTION

Inductively Coupled Plasma - Mass Spectrometry has been shown in Chapter 2 to produce lithium isotope ratio measurements with high precision. A calculated weighted, mean relative standard deviation, using 70 replicate measurements of 27 separate samples, was used to estimate the general precision obtainable in ICP-MS lithium isotope ratio measurements. This calculation estimates the precision with which measurements can generally be made, to be 0.08 %. In Chapter 3, the quantitative recovery of lithium after sample preparation was shown, with no detectable loss of lithium after ion exchange. High precision and quantitative recoveries, however, do not necessarily indicate a high degree of accuracy. Neither measures of precision or efficiency take into account any possible contribution of systematic error in the method. It is necessary, therefore, to have an independent assessment of the accuracy of the measurement protocol.

This chapter examines the absolute accuracy of the ICP-MS lithium isotope ratio measurement protocol described in Chapter 2, and describes the calibration of the sample preparation procedure for any introduction of systematic error. Systematic error in sample preparation can result from such things as; lithium contamination from reagents or

labware, loss of lithium during sample evaporation, incomplete recovery of lithium from columns, etc. In sample measurement procedures, such factors as; an incorrectly calibrated reference standard, dissimilar behaviour of samples and standard in the plasma, inapplicable blank subtraction, etc., may introduce systematic error into the measurement. In order to determine the absolute accuracy with which a measurement may be made, and to what degree if any, the measurement protocol is affected by systematic error, it is necessary to measure a substance with known isotopic composition using the protocol as it is applied to unknown samples, and then to compare the measured ratio with the known ratio of the substance.

Three substances with certified isotopic compositions were obtained for this study: the Li_2CO_3 standard IRM-016 which is used as the reference standard for all isotopic measurements performed herein; the Li_2CO_3 standard SVEC, which has the same origin as IRM-016 (i.e., Foote Minerals Co., King's Mountain North Carolina) but has a different certified isotopic composition; and, LE-7; lithium in the metal form which is highly enriched in the ^7Li isotope. In addition, two other materials were measured in this section; one to determine the consistency of this method with other published lithium isotope studies (SPEX, a spectroscopic lithium solution from Specpure company Ltd.), and the other to determine the uniformity in isotopic composition of material derived from the Foote Mine, King's Mountain North Carolina (FB.M2, a spodumene sample). All of these samples were measured using the protocol described in Chapter 2. The certificate values of the standards are summarized in Table 9, and the determined ratios for all of the

materials are summarized in Table 10. In addition to this, the sample preparation procedure was calibrated by using an aliquot of IRM-016 as a positive control, and subjecting it to the entire sample preparation and measurement protocol (sample I.D., CONTROL, in Appendix IV).

4.2 TERMINOLOGY

δ-Value: the δ notation indicates the deviation of a sample's isotopic composition from the composition of an isotopic reference standard in parts per thousand (i.e., per mil). δ-Values in this study were expressed with respect to the ^6Li isotope (Equation 8), and absolute isotope ratios are expressed as $^7\text{Li}/^6\text{Li}$ in keeping with the conventions used in the literature.

$$(8) \quad \delta^{6\text{Li}} (\text{‰}) = \frac{\frac{(^6\text{Li})}{(^7\text{Li})_{\text{sample}}} - \frac{(^6\text{Li})}{(^7\text{Li})_{\text{standard}}}}{\frac{(^6\text{Li})}{(^7\text{Li})_{\text{standard}}}} \times 1000$$

where, the standard used in all measurements was IRM-016.

Correction Factor: the instrumental response during ICP-MS is calibrated with the reference standard. A correction factor is calculated (Equation 6,

Chapter 2) based on this calibration, to compensate for instrumental mass discrimination. A correction factor is obtained for every experiment and applied to the unknown sample being measured.

Reference Standard: the reference standard refers to the standard used to calibrate the instrument response during ICP-MS measurements. In this study, standard IRM-016 [Central Bureau for Nuclear Measurements, Geel Belgium; Isotopic Reference Material #IRM-016 (Michiels and De Bièvre, 1983)] was used as the reference standard for all isotopic measurements.

4.3 CALIBRATION STANDARDS

4.3.1 - Certified Isotopic Standards

Table 9 lists the certified isotopic standards along with their certificate lithium isotopic values. Details of each standard is given below.

IRM-016

IRM-016 is a Li_2CO_3 sample purchased from the Central Bureau for Nuclear Measurements, Geel Belgium. This material, which originated from the Foote Mineral Co., Kings Mountain North Carolina, has been calibrated with primary standards by Michiels and De Bièvre 1983, using thermal ionization mass spectrometry. The Li_2CO_3

standard, IRM-016 has been rated the best measurement from a natural source for lithium by De Bievre et al. (1984). Based on this rating, and on the obvious quality of the work of Michiels and De Bievre, 1983, this material was selected as the reference standard for calibrating all isotope ratio measurements performed in this study. It has a certificate value of 12.29 ± 0.05 (Michiels and De Bievre, 1983).

SVEC

The Li_2CO_3 standard, SVEC, was obtained from Chalk River Nuclear Laboratories of Atomic Energy of Canada. It was first measured by Svec and Anderson in 1965, who found its ratio to be 12.22 ± 0.05 , and was later recalibrated with primary standards by Flesch et al., 1973, who certified its isotope ratio to be 12.02 ± 0.03 (Table 9). The standard was prepared from virgin spodumene ores obtained from the Foote Mineral Company, originating from the Foote Mine, Kings Mountain, North Carolina (Flesch et al., 1973). Although this aliquot is ~20 years old, the carbonate is non-hygroscopic and stable to 700°C (Flesch et al., 1973), and therefore should have a good "shelf life".

LE-7

LE-7 metal was purchased from U.S. Services Inc., Summit, N.J. The method of assay of the metal, and uncertainties were not reported on the certificate, however, its isotope ratio is calculated below based on the certified assay of the metal.

Assay:	99.95 % Lithium	Li-content:	⁷ Li	98.46 wt %
	0.05 % impurities		⁶ Li	1.54 wt %

Calculated Atomic Ratios:

$$\begin{array}{ll} \text{g/g } ^7\text{Li} & 0.995 \times 0.9846 = 0.98411 \\ \text{g/g } ^6\text{Li} & 0.995 \times 0.0154 = 0.01539 \end{array}$$

$$\begin{array}{ll} \text{mol/g } ^7\text{Li} & 0.98411/7.0097 = 0.14039 \\ \text{mol/g } ^6\text{Li} & 0.01539/6.0081 = 0.002562 \end{array}$$

$$\begin{array}{ll} \text{Molar Isotopic Ratio } ^7\text{Li}/^6\text{Li} & = 0.14039/0.002562 \\ & = 54.80 \end{array}$$

Since both SVEC and IRM-016 are calibrations of materials of the same origin, it is this metal which is used as an independent test of the accuracy of the developed lithium isotope ratio measurement protocol described in Chapter 2.

4.3.2 - Other Materials

SPEX Spectroscopic Standard

SPEX is a spectroscopic lithium solution (Specpure Co., Ltd.). It is certified as to concentration, but not as to isotopic composition. This standard has likely been depleted in ⁶Li for use in the Nuclear Industry (Cotton and Wilkinson, 1980). This standard has not been calibrated isotopically, but a published value appeared in the literature in 1991 (Vanhoe et al., 1991) in an ICP-MS lithium isotope study of biological materials. In that study, isotope ratios were obtained using the method of isotope dilution using ¹⁰Be, with only fair precision. The value obtained by Vanhoe et al. for the lithium spectroscopic

solution, is compared to the measured isotope ratio of the solution obtained with this method. In this fashion, the consistency of our method with other methods is determined. Both the published and the measured values for this solution are summarized in Table 10.

FB.M2, Spodumene from Foote Mine, Kings Mountain North Carolina

A natural spodumene crystal obtained from the Foote Mine, King's Mountain North Carolina was measured, and its isotope ratio was compared to both SVEC and IRM-016. Such a comparison was made to determine the uniformity of the isotopic composition of materials from this source, and to assess the credibility that two standards derived from materials originating in the Foote Mine, could have very different isotopic compositions.

4.3.3 - Measurement of Calibration Standards

Table 10 summarizes the values obtained from the measurement of the standards and materials described above. The standard IRM-016 is not included in Table 10 since it was used as the reference standard to which all measurements were corrected, however information relating to IRM-016 is given in Table 9. Table 9 summarizes the information available for certified isotopic standards used in this study. The other materials are compared in Table 10 to their certified or published values, except FB.M2 for which this information is not available.

From Table 10, we observe that the measured ratio for SVEC is very similar to the

value of the reference standard, IRM-016. Although these standards have different certificate values, both of these Li_2CO_3 preparations were obtained from the Foote Mineral Co., Kings Mountain, North Carolina, and derived from source materials (spodumene and petalite) from the Foote Mine. Calibrating SVEC with IRM-016 gives a ratio of 12.303 ± 0.019 . A third material obtained from the Foote Mine, spodumene sample FB.M2, was used to indicate the isotopic uniformity of materials from this source. The ratio obtained for FB.M2 was 12.308 ± 0.039 . This value is essentially equivalent to the SVEC standard's measured ratio. This evidence seems to suggest an isotopic uniformity of material derived from spodumene/petalite ore from the Foote Mine, King's Mountain North Carolina, which in turn would contra-indicate the veracity of two different certified isotopic compositions for material from this source. The large deviation reported for SVEC from its certified value, therefore, does not have any implications with regard to the accuracy of the measurement protocol. In fact, Svec et al., 1965, reported a value of 12.22 ± 0.05 for Li_2CO_3 obtained from the Foote Mineral Co. The indication is that the Flesch et al., 1973 calibration is invalid.

An indication of the accuracy of the method must, therefore, be obtained from the measurement of LE-7. The certified ratio of lithium-7 enriched material (LE-7) is calculated to be 54.80 (uncertainty unknown). Several determinations of the LE-7 isotope ratio were performed, each at a different ion intensity (cps) range. A mean of all eight determinations gives the value 54.47 ± 0.20 for the $^7\text{Li}/^6\text{Li}$ ratio of LE-7. Some of the determinations made for LE-7 were performed at ion intensities beyond the linear range of

the analytical calibration curve (Figure 8), contributing to the large RSD reported here. This is likely the cause of the somewhat low value, as a loss of sensitivity is experienced for ^7Li beyond the linear range, but not for ^6Li . The second ratio reported for LE-7 in Table 10 uses only those determinations performed in the ideal ion intensity range (Figure 9) to calculate the ratio. The value reported is 54.73 ± 0.01 . The absolute deviation of the measured ratio to the certificate value is -0.13% (i.e., -1.3‰). The absolute deviation from the certified value of LE-7 for this second value is taken to represent the accuracy of the method. In the optimum concentration range, therefore, the method is capable of producing ratio determinations with a 0.13% accuracy. In fact, even with non-ideal ion intensities, accuracy is still within 0.6% .

Finally, a value of $^7\text{Li}/^6\text{Li}$ of 18.05 ± 0.40 for the spectroscopic standard from Specpure Co., Ltd., was calculated from data presented in Vanhoe et al., 1991. The isotope ratio of 17.95 obtained in this study agrees with Vanhoe et al., 1991, to within the analytical uncertainty of their method.

4.4 METHOD CALIBRATION

The determinations in Table 10 were performed on pure lithium standards not requiring any sample preparation, except dissolution and dilution. The report of the accuracy obtained in the measurement of these standards therefore, is only indicative of the accuracy of the isotope ratio measurement protocol given in Chapter 2, and does not

reflect the absence of systematic error in the sample preparation procedure given in Chapter 3. Therefore, to ensure that the preparation procedure does not produce any isotopic shift in samples, the procedure was calibrated using an aliquot of IRM-016 as a positive control. The aliquot was put through the entire sample preparation procedure and then was measured using the measurement protocol. This CONTROL experiment, yielded a ratio of 12.300 ± 0.002 for the IRM-016 aliquot [certificate value: 12.29 ± 0.05 (Michiels and De Bievre, 1983; see Table 9)]. This value is within the estimated precision of our method of 0.08 %, and is within the analytical uncertainty of the certificate value for IRM-016. This evidence suggests that the sample preparation procedure does not cause any isotopic shift in samples.

4.5 SUMMARY AND CONCLUSIONS

Measurement of LE-7, indicates that lithium isotope ratios performed by ICP-MS using the protocol in Chapter 2, can be made with up to 1.3 ‰ accuracy. In fact, deviating from the preferred ion intensity range of lithium for ratio measurements (100,000 to 150,000 cps), only resulted in a degregation in the accuracy to 6 ‰. Complete details of each individual standard determination may be found in Appendix IV.3.

Calibration of the analytical method using IRM-016 as a positive control indicated that the sample preparation procedure does not introduce any systematic error to the

isotope ratios. The measured ratio for the CONTROL was 12.300 ± 0.002 , using IRM-016 as the reference standard. The expected value for CONTROL was 12.29. The absolute deviation from the expected value was 0.08 %, which is within the estimated precision of our method (i.e., estimated precision of method is 0.08 %).

Conclusions

1. SVEC, was found to be identical to IRM-016 in isotopic composition.
2. Determination of FB.M2, the spodumene sample from the Foote Mine, King's Mountain Carolina, gave a ratio equivalent to the two standards obtained from the Foote Mineral Co. (SVEC and IRM-016).
3. IRM-016 was used as the reference standard, to which all samples are calibrated, throughout the study.
4. The spectroscopic lithium solution (SPEX) from Specpure Chemicals Ltd., had a ratio of 17.95 ± 0.004 . This was compared to a reported literature value for this solution of 18.05 ± 0.40 (Vanhoe et al., 1991).
5. Measurement of LE-7 in the ideal ion intensity range (Figure 9) indicates an accuracy of 1.3 ‰ is possible for the measurement protocol.
6. Performance of a positive control experiment to calibrate the sample preparation procedure indicated that no isotopic shift occurs during sample preparation.

Table 9: Certified Isotopic Standards

Standard	Form	Supplier	Reference	Certified ³ $^7\text{Li}/^6\text{Li} \pm \sigma$
IRM-016	Li_2CO_3	P. De Bievre	1	12.29 ± 0.05
SVEC	Li_2CO_3	H.J. Svec	2	12.02 ± 0.03
LE-7	Metal	U.S. Services Inc., Summit, N.J.	Certificate	$54.80^{4,5}$

¹Michiels and De Bievre, 1983.

²Flesch et al., 1973.

³Atomic ratio.

⁴Calculated ratio based on certificate assay.

⁵Uncertainty unavailable.

Table 10: Measured Ratios of Standards Relative to IRM-016

Standard	Certified or Published Ratio	Measured Ratio ¹ ±STDS	n	Deviation from Published Value (‰)
SVEC	12.02 ± 0.03	12.30 ± 0.02	6	-22
FB.M2	n/a	12.31 ± 0.04	1	n/a
LE-7	54.80 ³	54.47 ± 0.20	8	+6.0
LE-7	54.80 ⁴	54.73 ± 0.01	2	+1.3
SPEX	18.05 ± 0.40 ²	17.95 ± 0.04	2	+5.5

¹Corrected using IRM-016 as the reference standard

²Not a certified value, published value from Vanhoe et al., 1991

³Replicate measurements were performed at a variety of concentrations

⁴Only ratios measured in the "optimum" concentration range are used for this calculation ("Optimum" meaning the range determined optimum for lithium isotope ratio measurements in Figure 9).

n/a indicates information not available.

**PART II - LITHIUM ISOTOPE STUDIES OF GEOLOGICAL
SAMPLES**

CHAPTER 5

PART II - INTRODUCTION

Unlike other light stable isotopes, the geochemistry of lithium isotopes is not well characterized. Natural lithium occurs as a mixture of two isotopes; lithium-7 and lithium-6 with respective proportions of 92.5 % and 7.5 % (Horlick et al., 1987). Lithium participates in numerous geochemical processes, and as with both lighter (H) and heavier (O, B, C) elements, useful geological information may potentially be extracted from the measurement of fractionation of Li-isotopes. The relatively large mass difference between the two lithium isotopes (>15 %) and their low mass make them favourable candidates to be influenced by isotope fractionation processes in nature.

Lithium is found ubiquitously in the lithosphere with an average distribution of 1-4 ppm in the mantle, 7-10 ppm in oceanic crust and 13-32 ppm in continental crust (Heier and Billings 1978). Granites and rhyolites in particular, have average lithium contents in the order of 30 to more than 50 ppm (Heier and Billings 1978), and rare element pegmatites can concentrate lithium in quantities up to >1 wt % (Cerny, 1991a). Lithium is also present in natural waters in low quantities; seawater containing approximately 0.2 ppm Li (Gyongyossy and Spooner, 1979), and freshwaters, less.

Several minerals concentrate lithium in their crystal structure, but the principal

ones, which are all found in granitic pegmatites, are spodumene (up to 3.7 wt % Li), petalite (up to 2.3 wt %), lepidolite (up to 3.2 wt % Li), amblygonite (up to 4.7 wt %) and eucryptite (5.5 wt %), (Klein and Hurlbut, 1985). Because of the small size of Li^+ with respect to the next alkali metal ion, Na^+ , only limited substitution of lithium for sodium in crystals occurs (Cocco et al., 1978), however, since Li^+ is closer to Al^{3+} , Fe^{2+} , and Mg^{2+} in radius, ionic substitution by lithium in crystal sites normally occupied by these ions is more prevalent (Cocco et al., 1978). With very few exceptions (i.e., cryolithionite, griceite, lithiophorite), Li-bearing minerals occur in nature as silicates or phosphates.

Isotope fractionation is possible in nature because of the differences in the kinetic and thermodynamic properties of the individual isotopes (Karplus and Porter, 1970). Fractionation of lithium isotopes in nature may be caused by several mechanisms, but predominantly by physicochemical processes such as: adsorption/desorption, fractional crystallization, solvation/precipitation, diffusion, and ion exchange (Gregoire, 1989a). The earliest lithium isotope study, performed in 1938 by Taylor and Urey, showed that substantial lithium isotope fractionation takes place during ion exchange. Measurable fractionation has also been observed during chemical precipitation (Cameron, 1955; Svec and Anderson, 1965), and associated with fractional crystallization (Svec and Anderson, 1965). Furthermore processes such as hydrothermal alteration (Divis and Clark, 1978), metasomatism, diffusion (Morozova and Alferovskiy, 1974), and low-temperature alteration (Chan et al., 1992), have all been reported to cause isotopic shifts in lithium compositions.

Most early studies were performed by conventional mass spectrometric techniques or by thermal ionization mass spectrometry. However, Flesch et al., 1973, and Michiels and De Bievre, 1983, caution that some early data may be unreliable, citing isotopic effects during chemical treatment or mass discrimination in the ion source as major contributing sources of error. [The technique described in Part I of this work, has been carefully calibrated with a secondary isotopic reference standard (Michiels and De Bievre, 1983), and is not subject to such difficulties]. After 1978, a 10-year hiatus exists in the lithium isotope literature, and since then, only three papers (Chan 1987, Chan and Edmond, 1988, Chan et al., 1992) have been published. Thus, in a broader sense, this work contributes to the overall understanding of the variation of the lithium isotope ratios in crustal rocks.

The general trends in lithium isotope systematics that have been identified in the literature are summarized as follows. ^6Li is preferentially taken up by clay minerals (Taylor and Urey, 1936) and by authigenic low-temperature alteration minerals (Chan et al., 1992). Further, systems that involve precipitation of a lithium-phase from a liquid, result in the precipitated phase being enriched in ^6Li and the solution phase being enriched in ^7Li (Oi et al., 1991a, 1991b; Cameron 1955). The mobilization of fluids by processes such as metamorphism and metasomatism results in the preferential partitioning of ^7Li into the fluid phase (Chan et al., 1992; Morozova and Alferovskiy, 1974), and finally, the most recent contribution to the literature on lithium isotope ratios in geoscience, investigates

relationships between lithium isotope ratios and seawater in MORB basalts (Chan and Edmond, 1988; Chan et al., 1992). Chan et al., 1992, found weathering processes between basalts and ocean water resulted in a mixing of the two reservoirs. The MORB reservoir has a fairly light isotopic signature [-3.4 to -4.7 ‰ relative to SVEC (see Chapter 4)], while the ocean reservoir has a heavy signature (-33.2 ‰). Weathered basalts became isotopically heavier as a result of their interaction with hot hydrothermal solutions derived from seawater. Chan et al., 1992 also identified fresh water reservoirs to have an isotopic composition in the order of -15.3 ‰ to -18.5 ‰, and occasionally heavier. The literature seems to support the very cursory observation that, in general, ^6Li seems to prefer crystal coordination, while ^7Li prefers solvation. This tendency would follow logically from the fact that the bond energy for ^6Li is higher than that of ^7Li in a given molecule (Karplus and Porter, 1970).

One very striking observation in the literature is that lithium isotope systematics seem to have inverse relationships with potassium (Oi et al., 1991a; Morozova and Alferovskiy, 1974), rubidium (Oi et al., 1991a), strontium (Plyusnin et al., 1978), and oxygen isotope systematics (this study). Oi et al., 1991a, have attributed this property of lithium with the isotope effect accompanying hydration of the ion.

The main objective of this study was to develop a method for the measurement of lithium isotope ratios by ICP-MS, and to perform isotopic studies on Li-minerals. In all, 55 samples of 18 different mineral species were measured. All but one of the 55 samples

were single crystals of Li-minerals. The obvious advantage of using this type of sample being, a) ease of mineral separation, and b) high lithium content, contributing to a simpler extraction of lithium from its matrix. The 55 minerals were studied with four objectives in mind. These objectives were: (1) to measure a large number of isotope ratios to estimate the natural range of variation of lithium abundance ratios in crustal rocks, (2) to examine pairs of coexisting minerals to observe the fractionation of lithium between them, (3) to examine a suite of spodumene samples to determine the relationship between mineral chemistry and isotopic composition, and 4) to study a suite of Li-micas from topaz rhyolites to observe the effect of magmatic degassing on the lithium isotope ratio, and to compare oxygen and hydrogen isotopic compositions of whole rock samples to the lithium isotopic compositions of the mica separates.

Samples for this study were donated by The Canadian Museum of Nature, Dr. F.W. Breaks, Dr. R.P. Taylor, Dr. Joan Carles Melgarejo (Barcelona University) and Dr. J. Van Velthuisen. Information on the origin of each sample, donator and brief hand specimen descriptions are given in Appendix II.

CHAPTER 6

LITHIUM ISOTOPE RATIOS OF MINERAL SAMPLES

6.1 INTRODUCTION

With few exceptions, the independent lithium minerals occur principally or exclusively in lithium-rich granitic pegmatites, or their exomorphic halos (London and Burt, 1982a). Granitic pegmatites generally occur in 'fields' with the lithium pegmatites being spatially located the farthest from the apparent thermal or magmatic source of all the pegmatites in the 'field' (Heinrich, 1953; Stewart, 1978). In addition, they are usually found intruding metamorphic terrains that have recorded steep thermal gradients (Cerny and Trueman, 1978). Many lithium pegmatites are sharply zoned in grain size and mineralogy, with lithium minerals being concentrated in the extremely coarse-grained interior zones or cores. Unzoned spodumene-bearing pegmatites are also fairly common (i.e., Kings Mountain, North Carolina) (Cerny, 1991b).

The majority of the samples used in this study were derived from pegmatite occurrences. Petalite, spodumene, amblygonite-montebrazite, and lithiophilite-triphyllite are generally held to be of primary origin (Cerny, 1991b), while, in contrast, lepidolite is arguably held to be secondary in origin (metasomatic) by some authors, but may be multi-generational (Cerny, 1991b). Li-micas may also be found in topaz granites (Taylor, 1992), and greisens (London and Burt, 1982b), and tourmalines and amphiboles occur in

the exomorphic halos around pegmatite intrusions (i.e., the result of metasomatism) (Cerny, 1991b). Bikitaite, hectorite and cookeite are also found in granitic pegmatites, but they occur in alteration assemblages. Lithiophorite often occurs in Mn-deposits, and is believed to form as the result of chemical precipitation from aqueous solution at low temperatures (Guilbert and Park, 1986). Finally, two of the samples, griceite and polyolithionite were found in pegmatites associated with a nepheline syenite intrusion (Van Velthuisen and Chao, 1989).

In this chapter, the data obtained from the measurement of these 55 mineral samples is presented. A cursory look at the isotopic data in the context of; (i) general range of ratios found, (ii) relationships between mineralogy and ratio, (iii) relationships between coexisting mineral pairs, and (iv) relationships between spodumene chemistry and isotopic composition.

6.2 TERMINOLOGY

δ -Value: For most geochemical purposes, knowledge of the difference in absolute isotopic ratios between two substances is more useful than quantifying the isotope ratio. The δ -Value then, is the relative difference in isotope ratio between a sample and a standard expressed in parts per thousand, or per mil (‰). δ -Values in this study were expressed with respect to the ^6Li isotope (Equation 8),

and absolute isotope ratios are expressed as $^7\text{Li}/^6\text{Li}$ in keeping with the conventions used in the literature. The δ -Value is given by:

$$(8) \quad \delta^{6\text{Li}} (\text{‰}) = \frac{\frac{(^6\text{Li})}{(^7\text{Li})_{\text{(sample)}}} - \frac{(^6\text{Li})}{(^7\text{Li})_{\text{(standard)}}}}{\frac{(^6\text{Li})}{(^7\text{Li})_{\text{(standard)}}}} \times 1000$$

where, the standard used in all measurements was IRM-016.

Negative δ -Values indicate that a sample is depleted in ^6Li relative to the standard, and positive values indicate that the sample is likewise enriched in ^6Li .

Observed per mil Fractionation Between Two Coexisting Phases (Δ): The *observed per mil fractionation* between two coexisting mineral phases is given by the difference in δ -Values of those two phases [Equation 9 (Faure, 1986)]. Under conditions of isotopic equilibrium, the observed per mil fractionation for a mineral pair, is approximately equal to the *equilibrium per mil fractionation* (Equation 10).

$$(9) \quad \Delta_{i-j} = \delta_i - \delta_j$$

$$(10) \quad \approx 1000 \ln \alpha_{(i-j)}$$

where α , the fractionation factor is equivalent to:

$$(10) \quad \alpha(i-j) = \frac{Ratio_i}{Ratio_j}$$

For two phases of fixed composition, α and $1000 \ln \alpha$ are a function of temperature (this relationship must be experimentally established for the two specific phases). As temperature increases, fractionations tend to decrease (i.e., $\Delta i-j$ values for specific mineral pairs decrease with increasing temperature).

6.3 INDIVIDUAL MINERAL SAMPLES

6.3.1 - Procedure

Fifty-five individual mineral samples from a variety of localities were donated for this study. Samples were separated from their matrix by hand, and crushed in an agate mortar and pestle. Crushed fragments were cleaned with de-ionized water and ethanol, and dried at 90 °C in clean glass beakers. Inclusion-free fragments of each sample were hand picked under a binocular microscope. These fragments were then powdered to ~200 mesh, weighed, and dissolved according to the procedure given in Appendix III. Dissolved samples were then put through the ion exchange procedure described in Chapter 3, to separate lithium from the rest of the matrix. Each sample aliquot used for

measurement came from a single crystal, except for the micas from Fawwarah, Saudi Arabia; Pleasant Ridge Pluton, N.B.; and St. Austell Pluton, Cornwall, England; which were mineral separates. Determinations of Li concentrations were performed using ICP-MS and isotope ratios were measured according to the protocol described in Chapter 2.

Table 12 summarizes the analytical results and Table 11 summarizes the geological information available for each sample. Ratio values given in Table 12 represent either single determinations or weighted averages of replicate measurements. Determinations were made on extremely small sample sizes (~30mg homogenized in solution), and therefore, because of the very coarse grain size of many of the samples, isotopic heterogeneity within a crystal may introduce some bias in some measurements. A complete set of ICP-MS data and hand specimen descriptions is located in Appendix IV and II, respectively.

In addition to this, thin sections were prepared for all of the spodumene samples, except ACL, and electron microprobe data were gathered for each sample using the experimental conditions described in Appendix V. A summary of the microprobe data is given in Table 14. Each entry in Table 14 represents an average of four point analyses from core to rim for a single spodumene thin section.

6.3.2 - Lithium Isotope Ratios - General

For the fifty-five samples measured, $\delta^6\text{Li}$ permil values ranged from +3.5 ‰ for

Table 11: Locality and Geological Setting Information for Samples

Sample #	Mineral Name	Locality	Location	Geological Setting	Age (b.y.)	Period
39403A	Amblygonite	Minas Gerais, Brazil	---	Granitic Pegmatite	2.3 - 2.5	Proterozoic
47726	Amblygonite	Bernic Lake, Manitoba	Tanco Mine	Granitic Pegmatite	2.6	Archaen
44757	Bikitaite	Kings Mountain, N. Carolina	Footo Mine	Granitic Pegmatite	0.40 - 0.27	Devonian-Permian
HECTORITE	Clay mineral	Yavapai County, Arizona	Lyles Mine	---	---	---
53407	Clinoholmquistite	Siberia, Russia	---	Granitic Pegmatite	---	---
43159B	Cookeite	Mount Mica, Maine	---	Granitic Pegmatite	0.4 - 1.7	Proterozoic-Devonian
43159A	Elbaite	Mount Mica, Maine	---	Granitic Pegmatite	0.4 - 1.7	Proterozoic-Devonian
43172	Elbaite	Kenora, Ontario	Lily Pad Pound Occurrence	Granitic Pegmatite	---	---
43182B	Elbaite	San Diego Co., California	---	Granitic Pegmatite	---	---
50914A	Elbaite	Minas Gerais, Brazil	Aricanga Mine	Granitic Pegmatite	2.3 - 2.5	Proterozoic
F90-15C	Elbaite	Mount Mica, Maine	---	Granitic Pegmatite	0.4 - 1.7	Proterozoic-Devonian
39403B	Eosphorite	Minas Gerais, Brazil	---	Granitic Pegmatite	2.3 - 2.5	Proterozoic
F86-59	Griceite	Mont St. Hilaire, Quebec	---	Sodalite Inclusions	0.09 - 0.13	L. Cretaceous
45181	Holmquistite	Lac Malartic, Quebec	---	Granitic Pegmatite	---	---
50597	Holmquistite	Brankruken, Austria	---	Granitic Pegmatite	---	---
1091	Lepidolite	St. Austell, England	St. Austell Pluton	Topaz Granite	0.28	E. Permian
1160	Lepidolite	St. Austell, England	St. Austell Pluton	Topaz Granite	0.28	E. Permian
2273	Lepidolite	St. Austell, England	St. Austell Pluton	Topaz Granite	0.28	E. Permian
43159C	Lepidolite	Mount Mica, Maine	---	Granitic Pegmatite	0.4 - 1.7	Proterozoic-Devonian
43182A	Lepidolite	San Diego Co., California	---	Granitic Pegmatite	---	---
50914B	Lepidolite	Minas Gerais, Brazil	Aricanga Mine	Granitic Pegmatite	2.3 - 2.5	Proterozoic
F90-15A	Lepidolite	Mount Mica, Maine	---	Granitic Pegmatite	0.4 - 1.7	Proterozoic-Devonian
38718	Lithiophilite	Bernic Lake, Manitoba	Tanco Mine	Granitic Pegmatite	2.6	Archaen
54134	Lithiophilite	Rio Grande do Norte, Brazil	Capoeira	Granitic Pegmatite	---	---
49684	Lithiophorite	Norman, Arkansas	North Mountain Mine	Mn-Deposit	---	---
51429	Petalite	Karibib, Namibia	Rubicon Mine	Granitic Pegmatite	0.8 - 1.7	Proterozoic
36660	Polythionite	Mont St. Hilaire, Quebec	Pegmatite Dike	Nepheline Syenite	0.09 - 0.13	L. Cretaceous
149-70	Siderophyllite	Eurajoki, Finland	Eurajoki pluton	Topaz Granite	1.57	Proterozoic
301-PL	Siderophyllite	Eurajoki, Finland	Eurajoki pluton	Topaz Granite	1.57	Proterozoic

Table 11 Cont'd: Locality and Geological Setting Information for Samples

Sample #	Mineral Name	Locality	Location	Geological Setting	Age (b.y.)	Period
ACL	Spodumene	---	Aclare Pegmatite	Granitic Pegmatite	---	---
FB.B1	Spodumene	Bearhead Lake Field, Ont.	Pakiagama Lake Peg.	Granitic Pegmatite	---	---
FB.C1	Spodumene	Crescent Lake Field, Ont.	Chappais Lake Peg.	Granitic Pegmatite	2.4 - 2.5	Proterozoic
FB.C2	Spodumene	Crescent Lake Field, Ont.	Teboshogeshik Peg. No. 2	Granitic Pegmatite	2.4 - 2.5	Proterozoic
FB.D1	Spodumene	Dryden Field, Ont.	Fairservice Peg. No. 1	Granitic Pegmatite	---	---
FB.D2	Spodumene	Dryden Field, Ont.	Fairservice Peg. No. 4	Granitic Pegmatite	---	---
FB.D3	Spodumene	Dryden Field, Ont.	Fairservice Peg. No. 11	Granitic Pegmatite	---	---
FB.D4	Spodumene	Dryden Field, Ont.	Gullwing Lake Peg.	Granitic Pegmatite	>2.7	Late Archean
FB.D5	Spodumene	Dryden Field, Ont.	Tot Lake Peg. 91-1	Granitic Pegmatite	>2.7	Late Archean
FB.D6	Spodumene	Dryden Field, Ont.	Tot Lake Peg. 91-2	Granitic Pegmatite	>2.7	Late Archean
FB.D7	Spodumene	Dryden Field, Ont.	Tot Lake Peg. 91-3	Granitic Pegmatite	>2.7	Late Archean
FB.D8	Spodumene	Dryden Field, Ont.	Tot Lake Peg. 91-4	Granitic Pegmatite	>2.7	Late Archean
FB.G1	Spodumene	Georgia Lake Field, Ont.	Nama Creek Peg.	Granitic Pegmatite	2.4 - 2.5	Proterozoic
FB.G2	Spodumene	Georgia Lake Field, Ont.	MNW Peg.	Granitic Pegmatite	2.4 - 2.5	Proterozoic
FB.M1	Spodumene	---	Ignace Peg.	Granitic Pegmatite	---	---
FB.M2	Spodumene	King's Mountain, N. Carolina	King's Mountain Pegmatite	Granitic Pegmatite	0.40 - 0.27	Devonian-Permian
FB.R1	Spodumene	Root Lake Peg. Field, Ont.	Roadhouse River Peg. No. 1	Granitic Pegmatite	---	---
FB.R2	Spodumene	Root Lake Peg. Field, Ont.	Roadhouse River Peg. No. 2	Granitic Pegmatite	---	---
38716	Triphylite	Newry, Maine	---	Granitic Pegmatite	0.4 - 1.7	Proterozoic-Devonian
38717	Triphylite	North Groton, N.H.	Palermo Mine	Granitic Pegmatite	---	---
82-5	Zinnwaldite	Pleasant Ridge, N.B.	Pleasant Ridge Pluton	Topaz Granite	0.36	L. Devonian
46801	Zinnwaldite	Zinnwald, Czech Republic	---	Topaz Granite	.305-295	E. Permian
181800	Zinnwaldite	Fawwarah, Saudi Arabia	---	Topaz Granite	0.59	L. Proterozoic
181878	Zinnwaldite	Fawwarah, Saudi Arabia	---	Topaz Granite	0.59	L. Proterozoic
181900	Zinnwaldite	Fawwarah, Saudi Arabia	---	Topaz Granite	0.59	L. Proterozoic
181904	Zinnwaldite	Fawwarah, Saudi Arabia	---	Topaz Granite	0.59	L. Proterozoic

--- indicates that information is not available

Table 12: Lithium Ratio and Concentration Data for Samples

Sample #	Mineral Name	Formula	n (1)	Corrected Ratio (2) ± Error (3)	Standard Error (3)	Wt % Li	ΔLi ± Error (3)	Standard Error (3)
39403A	Amblygonite	(Li,Na)AlPO ₄ (F,OH)	1	12.360 ± 0.021		4.10	-5.7 ± 1.7	
47726	Amblygonite	(Li,Na)AlPO ₄ (F,OH)	1	12.698 ± 0.021		4.62	-33.2 ± 1.7	
44757	Bikitaite	LiAlSi ₂ O ₆ ·H ₂ O	1	12.507 ± 0.006		3.71	-17.7 ± 0.5	
HECTORITE	Clay mineral	Na _{0.33} (Mg,Li) ₃ Si ₄ O ₁₀ (F,OH) ₂	5	12.291 ± 0.017		0.17	1.7 ± 1.4	
53407	Clinoholmquistite	Li ₂ (Mg,Fe ₂ +3Al ₂ Si ₈ O ₂₂ (OH) ₂	1	12.416 ± 0.045		0.57	-10.2 ± 3.6	
43159B	Cookeite	LiAl ₄ (Si ₃ Al)O ₁₀ (OH) ₈	1	12.424 ± 0.019		1.29	-10.9 ± 1.5	
43159A	Elbaite	Na(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	1	12.384 ± 0.027		0.72	-7.7 ± 2.2	
43172	Elbaite	Na(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	3	12.496 ± 0.010		0.50	-17.3 ± 0.8	
43182B	Elbaite	Na(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	3	12.351 ± 0.008		0.76	-4.1 ± 0.7	
50914A	Elbaite	Na(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	2	12.435 ± 0.007		0.77	-11.3 ± 0.6	
F90-15C	Elbaite	Na(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	4	12.407 ± 0.009		0.61	-10.3 ± 0.7	
39403B	Eosphorite	MnAlPO ₄ (OH) ₂ ·H ₂ O	1	12.282 ± 0.019		0.03	0.7 ± 1.6	
F86-59	Griceite	LiF	3	12.382 ± 0.028		n/a	-6.2 ± 2.3	
45181	Holmquistite	Li ₂ (Mg,Fe ₂ +3Al ₂ Si ₈ O ₂₂ (OH) ₂	2	12.306 ± 0.003		1.08	-1.1 ± 0.3	
50597	Holmquistite	Li ₂ (Mg,Fe ₂ +3Al ₂ Si ₈ O ₂₂ (OH) ₂	1	12.431 ± 0.040		0.44	-11.5 ± 3.2	
1091	Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	1	12.297 ± 0.002		2.17	-0.5 ± 0.2	
1160	Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	2	12.309 ± 0.002		2.19	-1.7 ± 0.2	
2273	Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	1	12.315 ± 0.025		2.02	-2.0 ± 2.0	
43159C	Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	1	12.337 ± 0.017		2.18	-3.9 ± 1.4	
43182A	Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	2	12.279 ± 0.003		2.08	1.1 ± 0.3	
50914B	Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	1	12.452 ± 0.031		2.47	-13.2 ± 2.5	
F90-15A	Lepidolite	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	2	12.354 ± 0.015		1.73	-6.6 ± 1.2	
CONTROL	Li-carbonate	Li ₂ CO ₃	2	12.300 ± 0.002		18.81	-0.7 ± 0.1	

Table 12 Cont'd: Lithium Ratio and Concentration Data for Samples

Sample #	Mineral Name	Formula	n (1)	Corrected Ratio (2) ± Standard Error (3)	Wt % Li	Standard Delt6Li ± Error (3)
38718	Lithiophilite	LiMnPO4	1	12.407 ± 0.026	3.84	-9.5 ± 2.1
54134	Lithiophilite	LiMnPO4	1	12.349 ± 0.010	4.31	-4.8 ± 0.8
49684	Lithiophorite	(Al,Lj)MnO2(OH)2	3	12.250 ± 0.020	0.68	3.5 ± 1.6
51429	Petalite	LiAlSi4O10	1	12.432 ± 0.035	1.97	-11.6 ± 2.8
36660	Polyolithionite	KLi2AlSi4O10	1	12.404 ± 0.039	2.60	-9.3 ± 3.2
149-70	Siderophyllite	KFe2(2+)Al3Si2O10(F,OH)2	2	12.325 ± 0.010	0.48	-3.2 ± 0.8
301-PL	Siderophyllite	KFe2(2+)Al3Si2O10(F,OH)2	1	12.307 ± 0.024	0.52	-1.4 ± 1.9
ACL	Spodumene	LiAlSi2O6	2	12.316 ± 0.012	3.70	-2.8 ± 1.0
FB.B1	Spodumene	LiAlSi2O6	1	12.298 ± 0.014	3.33	-0.6 ± 1.2
FB.C1	Spodumene	LiAlSi2O6	2	12.495 ± 0.002	3.37	-16.4 ± 0.2
FB.C2	Spodumene	LiAlSi2O6	4	12.523 ± 0.017	3.71	-18.5 ± 1.4
FB.D1	Spodumene	LiAlSi2O6	2	12.336 ± 0.004	3.46	-3.4 ± 0.3
FB.D2	Spodumene	LiAlSi2O6	2	12.387 ± 0.005	3.35	-8.1 ± 0.4
FB.D3	Spodumene	LiAlSi2O6	2	12.328 ± 0.002	3.39	-3.0 ± 0.1
FB.D4	Spodumene	LiAlSi2O6	1	12.338 ± 0.006	3.46	-3.9 ± 0.5
FB.D5	Spodumene	LiAlSi2O6	1	12.441 ± 0.014	3.40	-12.3 ± 1.1
FB.D6	Spodumene	LiAlSi2O6	1	12.440 ± 0.012	3.42	-12.2 ± 0.9
FB.D7	Spodumene	LiAlSi2O6	1	12.446 ± 0.021	3.56	-12.7 ± 1.7
FB.D8	Spodumene	LiAlSi2O6	2	12.417 ± 0.005	3.53	-10.2 ± 0.4
FB.G1	Spodumene	LiAlSi2O6	2	12.329 ± 0.007	3.35	-2.6 ± 0.5
FB.G2	Spodumene	LiAlSi2O6	2	12.375 ± 0.002	3.37	-6.8 ± 0.2
FB.M1	Spodumene	LiAlSi2O6	1	12.395 ± 0.021	3.46	-8.5 ± 1.7
FB.M2	Spodumene	LiAlSi2O6	1	12.308 ± 0.039	3.46	-1.5 ± 3.2

Table 12 Cont'd: Lithium Ratio and Concentration Data for Samples

Sample #	Mineral Name	Formula	n (1)	Corrected Ratio (2)	Standard Error (3)	Wt % Li	Delt 6Li ±	Standard Error (3)
FB.R1	Spodumene	LiAlSi ₂ O ₆	1	12.328 ±	0.022	3.08	-3.1 ±	1.8
FB.R2	Spodumene	LiAlSi ₂ O ₆	1	12.383 ±	0.076	3.51	-7.6 ±	6.1
38716	Triphylite	LiFe ₂ +PO ₄	2	12.315 ±	0.011	4.13	-2.7 ±	0.9
38717	Triphylite	LiFe ₂ +PO ₄	3	12.294 ±	0.005	3.89	-0.3 ±	0.4
82-5	Zinnwaldite	KLiFe ₂ +Al ₂ Si ₃ O ₁₀ (F,OH) ₂	2	12.346 ±	0.002	1.47	-4.5 ±	0.2
46801	Zinnwaldite	KLiFe ₂ +Al ₂ Si ₃ O ₁₀ (F,OH) ₂	1	12.370 ±	0.025	0.39	-6.5 ±	2.0
181800	Zinnwaldite	KLiFe ₂ +Al ₂ Si ₃ O ₁₀ (F,OH) ₂	1	12.349 ±	0.011	0.69	-4.8 ±	0.9
181878	Zinnwaldite	KLiFe ₂ +Al ₂ Si ₃ O ₁₀ (F,OH) ₂	1	12.393 ±	0.019	0.89	-8.4 ±	1.6
181900	Zinnwaldite	KLiFe ₂ +Al ₂ Si ₃ O ₁₀ (F,OH) ₂	1	12.344 ±	0.022	0.83	-4.4 ±	1.8
181904	Zinnwaldite	KLiFe ₂ +Al ₂ Si ₃ O ₁₀ (F,OH) ₂	1	12.348 ±	0.019	1.37	-4.7 ±	1.6

n = number of replicates averaged

(1) one replicate is made up of a block of 2-6 consecutive ratio measurements

(2) 7Li/6Li ratio corrected using IRM-016 as the reference standard

(3) calculation of standard error is given in Appendix I

a lithiophorite sample (#49684, Table 12), to -33.2 ‰ for an amblygonite sample (#47726, Table 12), relative to IRM-016. In Figure 19, samples are arranged into mineral groups, with the measured $\delta^6\text{Li}$ range for each group plotted. Figure 19 shows that the phosphates, as a group, span the widest range of $\delta^6\text{Li}$ values, and that the oxides and the halides, in general, have the lightest isotopic compositions. The remaining four groups have very similar $\delta^6\text{Li}$ ranges, with a large degree of overlap between each of the groups.

In Figure 20, individual mineral ranges of $\delta^6\text{Li}$ (IRM) are plotted. The column on the right hand side of the figure indicates the number of samples that have been measured to calculate each range. From this diagram, it can be seen that amblygonite spans the largest range of values (27.5 ‰), while the other phosphates, lithiophilite and triphylite, cover only limited ranges (i.e., <4 ‰). Although only two samples of each phosphate were measured, it still may be a valid observation that the amblygonite field and the triphylite field do not overlap. Elbaite, lepidolite and spodumene all cover large ranges (13-18 ‰), which overlap with one another to a large degree. This may be attributable to any number of causes. Interestingly, however, six samples of zinnwaldite cover only a very narrow isotopic range (<4 ‰). This is interesting in light of the fact that the occurrence of zinnwaldite is confined to greisens. Finally, lithiophorite and eosphorite, minerals of low temperature origin, both have positive $\delta^6\text{Li}$ (IRM) values (Figure 20). Positive $\delta^6\text{Li}$ values seem to be rare in minerals of magmatic origin based on this study. In the following sections, each mineral type will be dealt with in more detail.

Figure 19: Range of $\delta^6\text{Li}$ (relative to IRM) by mineral group.

Figure 20: Range of $\delta^6\text{Li}$ by mineral species. The number of samples measured to obtain each range is shown in the right hand column of the figure.

6.3.3 - Hydroxides, Halides, Hydrated Minerals

Figure 21 plots the $\delta^6\text{Li}$ values of this group plus hectorite and cookeite as a function of wt % Li. A decrease in Li content roughly corresponds to a trend towards lighter isotopic composition. All of the samples on Figure 21, except lithiophorite, are secondary minerals which have relatively low temperatures of formation compared to primary magmatic minerals.

Bikitaite

Bikitaite, $\text{LiAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, belongs to the Zeolite group. It occurs in lithium-rich pegmatites at temperatures below 350 °C (Drysdale, 1975). The occurrence of zeolites in pegmatites indicates low-grade "zeolite" metamorphism (Klein and Hurlbut, 1985, London, 1990, Foord, 1977, London, 1992). Bikitaite has a chemical formula identical to spodumene plus one water molecule per formula. The structure however, is a framework structure with water molecules held in the voids of the framework (Klein and Hurlbut, 1985). The water may be liberated from the framework on heating without disrupting the crystal structure. It has a theoretical maximum lithium component of 3.4 wt % Li. Our Bikitaite sample contained 3.71 wt % Li which suggests a complete dehydration of the sample. In addition, the Bikitaite sample (#44757) has a measured $\delta^6\text{Li}$ value of -17.7 ‰.

Eosphorite

Eosphorite, $\text{MnAl}(\text{PO}_4)(\text{OH})_2 \cdot \text{H}_2\text{O}$, is from the Childrenite-Eosphorite series and

occurs in pegmatites as an alteration product of amblygonite. Lithium is only a minor element in eosphorite, sample #39403B containing only 0.03 wt % Li. The replacement reaction which forms eosphorite involves a combination of hydration, oxidation and metasomatic exchange between amblygonite and fluid (London, 1990). Eosphorite, is clearly a secondary alteration product, and contains lithium as a result of the incomplete substitution $\text{Li}^+ \leftrightarrow \text{Mn}^{2+} + \text{OH}^-$ (London, 1990). It occurs as a fine powdery coating on the amblygonite sample #39403A, and has a positive $\delta^6\text{Li}$ value of +0.7 ‰.

Griceite

Griceite, LiF, is found in sodalite inclusions near the periphery of massive hornfels in Mt. St. Hilaire, Quebec, where it often occurs as cores of villiaumite (NaF) crystals. Griceite is a member of the halite group and has an ideal formula of LiF, with Li in octahedral coordination. The Li-F bond in griceite, is nearly purely ionic, and is very strongly held (Van Velthuisen and Chao, 1989). Griceite has never been found at any other locality, and there are very few known samples, although LiF is easily synthesized in the laboratory. Ideal composition would give a lithium component of 26.8 wt %, but a determination was not made for wt % Li for this sample, due to the fact that it was impossible to separate griceite from the accompanying villiaumite. Sample # F86-59 had a $\delta^6\text{Li}$ value of -6.3 ‰.

Lithiophorite

This is the only hydroxide sample measured in this study. Lithiophorite,

Hydroxides, Hydrated Minerals

Figure 21: $\delta^6\text{Li}$ as a function of wt % Li for lithiophorite and alteration minerals.

$(\text{Al,Li})\text{MnO}_2(\text{OH})_2$, is common in Mn-deposits, and may contain up to 2.5 wt % Li.

Sample # 49684 contains only 0.68 wt % Li and has a $\delta^6\text{Li}$ value of +3.5 ‰. The $\delta^6\text{Li}$ value for this sample is the most positive of all those listed in Table 12.

6.3.4 - Phosphates

Figure 22 displays the relationship between $\delta^6\text{Li}$ values and wt % Li for phosphates. The trend is similar to that in Figure 21, in that wt % Li is roughly decreasing as isotopic composition gets lighter. It is unclear from the diagram, however, if lithiophilite follows this trend.

Amblygonite

Amblygonite, $\text{LiAl}(\text{PO}_4)\text{F}$, is the pure lithium end-member name of the Amblygonite-Montebbrasite series. The series is a solid solution using the substitution $\text{Li}^+ + \text{F}^- \leftrightarrow \text{Na}^+ + \text{OH}^-$ (London and Burt, 1982b) between members. The name 'amblygonite' refers to the mineral of this series with $\text{F} > \text{OH}$. Amblygonite is found in granitic pegmatites (Klein and Hurlbut, 1987), where its presence indicates a high $f(\text{O}_2)$ (London and Burt, 1982b). The ideal formula contains 4.69 wt % Li, with lithium in 5-coordination (Klein and Hurlbut, 1987). Sample #39403A has 4.10 wt % Li and a $\delta^6\text{Li}$ value of -5.7 ‰, while sample #47726 contains 4.62 wt % Li and has the lowest $\delta^6\text{Li}$ value measured in this study of -33.2 ‰.

Phosphates

Figure 22: $\delta^6\text{Li}$ as a function of wt % Li for phosphates. The dashed line has been drawn through the two amblygonite samples.

Lithiophilite-Triphylite

All of the lithiophilite-triphyllite samples were from granitic pegmatites.

Lithiophilite-triphyllite, (LiMnPO_4 - $\text{LiFe}^{2+}\text{PO}_4$), is a primary mineral in pegmatites, but is readily altered by residual pegmatitic fluids (London and Burt, 1982a). Although Na substitution for Li towards the isostructural end-member natrophilite (NaMnPO_4) (London and Burt, 1982a) is possible, quite often, only trace amounts of Na are contained in lithiophilite (London and Burt, 1982a). With ideal compositions, lithiophilite and triphyllite contain 4.4 wt % Li. The details for each sample are found in Table 12, but the measured concentrations for our samples ranged from 3.84 wt % Li to 4.31 wt % Li. Triphyllite, being the Fe-rich end member will crystallize first in the pegmatite's history. Perhaps interesting to note is that the two triphyllite samples had lighter isotopic compositions (-0.3 to -2.7 ‰) than the two lithiophilite samples (-4.8 to -9.5 ‰).

6.3.5 - Phyllosilicates

The ideal mica has a formula of $\text{X}^{\text{XII}}\text{Y}_{2-3}\text{T}_4^{\text{IV}}\text{O}_{10}(\text{OH}, \text{F})_2$. Lithium occurs in the Y-site in 6-fold coordination, either as a major (zinnwaldite, lepidolite) or minor (siderophyllite) constituent. All of the lithian micas in this study are trioctahedral (since all three of the octahedral sites are filled). Li-Al micas can be either secondary metasomatic products generated by the action of late F-bearing aqueous fluids of early lithium aluminosilicates and K-feldspars, or "primary" phases which do not replace any pre-existing minerals (Stewart, 1978; Hawthorne and Cerny, 1982), and may be found in granitic pegmatites and Li-rich granites and greisens, and in exomorphic halos caused by

pneumatolytic alteration. Figures 23 and 24 plot the phyllosilicate samples on the wt % Li versus $\delta^6\text{Li}$ (‰) axes. In Figure 23, all Li-micas with <1.6 wt % Li are shown. Li-micas with this composition show no obvious relationship between the two variables on the plot, but in Figure 24, where all of the micas with >1.6 wt % Li are plotted, a general trend of decreasing lithium content with decreasing $\delta^6\text{Li}$ value, similar to that of Figures 21 and 22, is observed. Although cookeite and hectorite are phyllosilicates, they are plotted on Figure 21 with the 'alteration' minerals.

Cookeite

Sample 43159B is a cookeite sample from Mount Mica which coexisted with lepidolite and elbaite. Cookeite, $\text{LiAl}_4(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$, belongs to the chlorite group and has a formula of $\text{LiAl}_4(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ of the general form $\text{A}_{3-6}\text{Z}_4\text{O}_{10}(\text{OH})_8$. Lithium occurs in the A-site (Klein and Hurlbut, 1985) in octahedral coordination, where the principal substitution is $3\text{Li} \leftrightarrow \text{Al}^{3+}$, from the non-pegmatitic dioctahedral Al-chlorite donbassite. The theoretical maximum lithium composition for cookeite is 1.3 wt %. Sample 43159B contained 1.29 wt % Li and had a $\delta^6\text{Li}$ value of -10.9 ‰. In general, cookeite occurs in lithium-rich granite pegmatites and is often an alteration product of spodumene (Cerny, 1972; Quesnel, 1938), lepidolite or tourmaline (Foord, 1977, Hawthorne and Cerny, 1982). In sample 43159B, cookeite possessed a crustiform habit and occurred interstitial to lepidolite crystals and encrusting euhedral tourmaline. In any case, cookeite is often observed as a "very late" mineral (Hawthorne and Cerny, 1982).

Hectorite

Hectorite is a trioctahedral clay mineral of the smectite group (Newman, 1987) containing up to 0.47 wt % Li. Hectorite, $\text{Na}_{0.33}(\text{Mg,Li})_3\text{Si}_4\text{O}(\text{FOH})_2$ contains essential Li and F (Newman, 1987), with Li substituting for divalent cations in octahedral coordination, resulting in a net negative charge on the layers (Newman, 1987). In general, hectorite is formed under the conditions of low temperature alteration. Sample HECT had a Li content of 0.17 wt %, and had a $\delta^6\text{Li}$ value of +1.7 ‰.

Lepidolite

Lepidolite is a lithium mica of the Muscovite-Lepidolite series. There are two principal mechanisms whereby Li can substitute at the octahedral sites in the dioctahedral muscovite structure:

Li and F are very strongly correlated in natural compositions (Hawthorne and Cerny, 1982). Commonly, Li-Al micas with less than 1.6 wt % Li are characterized as "lithian muscovite", those which contain between 1.6 wt % Li and 2.1 wt % are transitional micas which contain some muscovite component, and true lepidolites are those which have greater than 1.9 wt % Li (Hawthorne and Cerny, 1982). The range in measured Li compositions for lepidolite samples was 1.73 to 2.47 wt % Li, and the range in $\delta^6\text{Li}$ values was +1.1 to -13.2 ‰. This is a fairly wide range compared with the minerals measured so far.

Polyolithionite

Polyolithionite is the end-member of the muscovite-lepidolite series at the lepidolite end. The polyolithionite (end member) is typical of silica-undersaturated alkali syenite pegmatites rather than granitic types (Hawthorne and Cerny, 1982). The sample in Figure 24 was from a nepheline syenite, Mt. St. Hilaire, Quebec. It has a Li wt % of 2.60, and a $\delta^6\text{Li}$ value of -9.3 ‰.

Zinnwaldite-Siderophyllite

Zinnwaldite had the narrowest range of $\delta^6\text{Li}$ values for a data set of more than two samples (-4.4 ‰ to -8.4 ‰) (see Figure 20). Zinnwaldite is a common mineral in Li and F-rich greisens and cassiterite-quartz veins, but is rare in lithium-rich granitic pegmatites (London and Burt, 1982b; Hawthorne and Cerny, 1982). However, Hawthorne and Cerny, 1982 state that zinnwaldite "... seems to be typical of Li-poor pegmatites, being the only Li-bearing species in them". The mechanism whereby Li substitutes at the octahedral sites in the trioctahedral structure is: ${}^{\text{VI}}\text{Li} + {}^{\text{IV}}\text{Al} \leftrightarrow {}^{\text{VI}}\text{Fe}^{2+} + {}^{\text{IV}}\text{Al}$ (Hawthorne and Cerny, 1982). Li and F are not as well correlated for this series as compared with the muscovite-lepidolite series, but F is always in excess of Li. The term zinnwaldite has been applied here to micas with only minor Li contents (0.39 wt % to 1.47 wt %; Table 12). Most of the zinnwaldite samples listed in Table 12, were from topaz granites in Fawwarah, Saudi Arabia.

Li-mica, Siderophyllite, Zinnwaldite

Figure 23: $\delta^6\text{Li}$ as a function of lithium content for Li-micas with less than 1.6 wt % Li.

Li-mica (Lepidolite, Polyolithionite)

Figure 24: $\delta^6\text{Li}$ as a function of lithium content for Li-micas with more than 1.6 wt % Li.

6.3.6 - Borosilicates

Figure 25 plots the lithium content of tourmalines versus isotopic composition. All of the samples plotted on Figure 25 are of the elbaite variety. A definite trend of increasing $\delta^6\text{Li}$ values with increasing wt % Li is evident. This trend opposes the trends indicated in Figures 21, 22, and 24.

Tourmaline (Elbaite)

Elbaite, the Li-end member of the elbaite-liddicoatite and dravite-elbaite tourmaline series', may occur in Li-rich granitic pegmatites (Roberts, 1990), or may be of late-stage metasomatic origin related to the emplacement of pegmatites (Thomas and Spooner, 1988). All samples on Figure 25 are of the Rubellite variety, except for sample #43159A which is a multi-coloured zoned tourmaline. Li occurs in six-fold coordination (octahedral) between Si_6O_{18} rings and BO_3 groups, in the Y-site of the general formula: $\text{XY}_3\text{Z}_6(\text{BO}_3)\text{Si}_6\text{O}_{18}(\text{O},\text{OH})_3(\text{OH},\text{F})$. The principal substitutions occurring in the tourmaline series' are: $\text{Li} + \text{Al} \leftrightarrow \text{Fe} + \text{Mg}$ (Klein and Hurlbut, 1985; Staatz et al., 1955; Foord, 1977), and $\text{Na} + \text{Al} \leftrightarrow \text{Ca} + 2\text{Li}$ (London and Burt, 1982a), and elbaite may theoretically contain up to 1.2 wt % Li. Our samples had lithium contents in the range of 0.50 to 0.77 wt % Li. From Figure 25, it can be seen that Li-tourmalines may possess a wide range both of $\delta^6\text{Li}$ values (-4 ‰ to -17.3 ‰), and that these values increase with increasing lithium content.

The lithium isotope geochemistry of tourmalines may prove to be useful in the

Figure 25: Lithium content as a function of isotope composition for tourmalines.

future for the study of metasomatism related to pegmatite intrusion (Thomas and Spooner, 1988). In granitic systems, tourmalines both reflect the composition of the fluid from which they crystallize (Glebov et al., 1975; Manning, 1982; Jolliff et al, 1986a, 1986b and 1987, among others), and are particularly resistant to subsequent alteration (Hansen, 1978). Coupled with the recent success of B isotopic studies of fluid evolution during pegmatite emplacement (Bryerley and Palmer, 1991; Clarke et al., 1989), this proposition seems highly favourable.

6.3.7 - Aluminosilicates

Amphiboles

Holmquistite is a lithium amphibole which occurs at or near contacts between lithium-rich pegmatites and country rocks of mafic composition (Roberts, 1990). [Clinoholmquistite is dimorphous with holmquistite, and sample #53407 from Siberia, occurs in crystals partly replaced by holmquistite (Roberts, 1990)]. Metasomatism due to pegmatite emplacement is responsible for the crystallization of holmquistite (London, 1986), where it preferentially replaces hornblende, or less commonly, biotite in mafic wall rocks and xenoliths (London and Burt, 1982a). Lithium is present as an important cation in the B (M4) site of the general formula:

where it occurs in 6-8 fold coordination. According to the nomenclature rules for amphiboles, as compiled by Bernard E. Leake, 1978, Li should compose no less than 1.0 wt % (1.7 wt % Li₂O), and may comprise up to 1.8 wt % Li (theoretically) of the

Figure 26: Lithium content as a function of isotope composition for amphiboles.

mineral in order to apply the series names holmquistite or clinoholmquistite. The mineral names shown on Figure 26, are the names ascribed by the Canadian Museum of Nature to their samples. The Leake (1978) classification requires that samples #53407 and 50597 be classified as a "lithian" amphiboles.

Figure 26 shows the relationship between $\delta^6\text{Li}$ values and wt % Li in the three amphibole samples measured. The Holmquistite sample (#45181) which contains > 1 wt % Li, has a $\delta^6\text{Li}$ value of -1.1 per mil. The other two amphibole samples, which contain less than 0.6 wt % Li, have $\delta^6\text{Li}$ values of -10.2 (#53407) and -11.5 (#50597). A very striking trend towards increasing $\delta^6\text{Li}$ values with increasing lithium content is observed in this figure. This is very similar to the trend observed for tourmalines. It is interesting to note, that both of these minerals are related to wall-rock alteration by late-stage metasomatic fluids during pegmatite emplacement.

Petalite

Petalite is a feldspathoid, which contains lithium (up to 2.27 wt %) in tetrahedral coordination with oxygen. Most petalites show only slight deviations from the ideal formula $\text{LiAlSi}_4\text{O}_{10}$ (London and Burt, 1982a). Petalite occurs as large crystals principally in the inner parts of zoned pegmatites (London and Burt, 1982a). The presence of petalite is indicative of a relatively low pressure of emplacement (Hawthorne and Cerny, 1982). Sample #51429 contains 1.97 wt % Li and has a $\delta^6\text{Li}$ value of -11.6 ‰.

Spodumene

Spodumene is a clinopyroxene with the general formula XYZ_2O_6 , where Li occupies the X-site (M2) in eight-fold coordination. Ideal spodumenes contain 3.7 wt % Li, and most natural spodumenes approach the ideal composition (but they may contain up to about 2 wt % of impurities, most notably Na, Mn and Fe). Na and Mn substitute in the M2-site, and most of the Fe substitutes for Al in the M1site (Klein and Hurlbut, 1985). Early-crystallizing spodumenes are the most Fe-rich, whereas later-stage primary crystals are relatively pure. The geochemistry of all spodumene samples is dealt with in more detail in the next section.

6.4 SPODUMENE CHEMISTRY

6.4.1 - Introduction

All of the spodumene samples were donated by F. W. Breaks. They were collected from various pegmatite fields of two main types: Type 1 - albite-spodumene type, or Type II - complex zonal type. Table 13 summarizes the lithium isotope data for these spodumenes. All of the samples are primary minerals, with the exception of FB.G2, from the MNW pegmatite which is a secondary replacement mineral.

The Tot Lake pegmatites (including Gullwing Lake) represent one of the most chemically evolved granitoid rock-suites in the Superior province; closely approaching the Tanco pegmatite (Cerny et al., 1981, Breaks, 1989). The Gullwing lake group, including

Table 13: Lithium Isotope ratios for Spodumene from Various Pegmatite Fields

Sample Number	Pegmatite	Measured Ratio $\pm\sigma^1$	Weight ² % Li	$\delta^6\text{Li} \pm \sigma$ (‰) ³
Type I: Albite-Spodumene Type Pegmatites				
FB.C1	Tebishogeshik #2	12.495 $\pm$ 0.002	3.37	-16.4 $\pm$ 0.2
FB.C2	Chappais Lake	12.523 $\pm$ 0.017	3.71	-18.5 $\pm$ 1.4
FB.D1	Fairservice #1	12.336 $\pm$ 0.004	3.46	-3.4 $\pm$ 0.3
FB.D2	Fairservice #4	12.387 $\pm$ 0.005	3.35	-8.1 $\pm$ 0.4
FB.D3	Fairservice #11	12.328 $\pm$ 0.002	3.39	-3.0 $\pm$ 0.1
FB.D4	Gullwing Lake	12.338 $\pm$ 0.006	3.46	-3.9 $\pm$ 0.5
FB.G1	Nama Creek	12.329 $\pm$ 0.007	3.35	-2.6 $\pm$ 0.5
FB.M1	Ignace Pegmatite	12.395 $\pm$ 0.021	3.46	-8.5 $\pm$ 1.7
FB.M2	King's Mountain	12.308 $\pm$ 0.039	3.46	-1.5 $\pm$ 3.2
FB.R1	Roadhouse #1	12.328 $\pm$ 0.022	3.08	-3.1 $\pm$ 1.8
FB.R2	Roadhouse #2	12.383 $\pm$ 0.076	3.51	-7.6 $\pm$ 6.1
Type II: Complex Zoned Pegmatites				
FB.B1	Pakiagama	12.298 $\pm$ 0.014	3.33	-0.6 $\pm$ 1.2
FB.D5	Tot Lake 91-1	12.441 $\pm$ 0.014	3.40	-12.3 $\pm$ 1.1
FB.D6	Tot Lake 91-2	12.440 $\pm$ 0.012	3.42	-12.2 $\pm$ 0.9
FB.D7	Tot Lake 91-3	12.446 $\pm$ 0.021	3.56	-12.7 $\pm$ 1.7
FB.D8	Tot Lake 91-4	12.417 $\pm$ 0.005	3.53	-10.2 $\pm$ 0.4
FB.G2 ⁴	MNW Pegmatite	12.375 $\pm$ 0.002	3.37	-6.8 $\pm$ 0.2

¹ σ Represents the standard error.²Lithium concentrations were determined by ICP-MS using external calibration with a spectroscopic standard (SPEX).³Ratios relative to the standard IRM-016.⁴Secondary replacement mineral.

Tot Lake, are metaluminous to weakly peraluminous, late to post-tectonic granitic pegmatites (Breaks and Janes, 1991). The Mavis Lake group, which includes the Fairservice pegmatites, are peraluminous post tectonic pegmatites derived from metasediments.

6.4.2 - Spodumene Crystal Chemistry

Electron microprobe analyses were performed on each spodumene sample. Table 14 summarizes the data (a complete set of data is located in Appendix V). In Figures 28 and 29, the electron microprobe data are compared to $\delta^6\text{Li}$ values. In Figure 27, spodumene chemistry is related to crystal colour. Examining suites such as this (i.e., composed of a single mineral) eliminates the influence of crystallographic controls on the lithium isotope composition of the samples, and thus, permits the results to be interpreted with respect to bulk chemical controls of isotopic compositions and the effects of post-magmatic (i.e., secondary) processes on isotopic compositions.

Figure 27 is a plot of $\log \text{Mn/Fe}$ versus Na content (in wt %) for the spodumenes examined in this study. The field of the graph was divided into three areas on the basis of colour. Spodumenes with relatively low sodium are white, while spodumenes plotting in the lower right corner of the graph are green. Spodumenes plotting in the central area are pink to pinkish brown in colour. No variation was observed between isotope ratio and colour however.

Table 14: Summary of Electron Microprobe Data for Samples

	B1 AVG	C1 AVG	C2 AVG	D1 AVG	D2 AVG	D3 AVG	D4 AVG	D5 AVG	D6 AVG	D7 AVG	D8 AVG	G1 AVG	G2 AVG	H1 AVG	R1 AVG	R2 AVG
SiO2	64.278	64.383	64.410	66.770	63.540	64.078	63.693	64.555	64.075	64.250	66.528	66.310	64.468	64.818	66.233	64.953
Al2O3	27.578	26.805	26.273	27.383	27.505	26.188	27.535	26.900	27.640	27.708	27.500	27.063	27.628	26.574	27.283	27.136
Fe2O3	0.080	1.023	1.355	0.628	0.268	1.520	0.463	0.288	0.238	0.018	0.340	0.900	0.015	0.946	0.478	0.315
MnO	0.040	0.165	0.260	0.113	0.070	0.130	0.075	0.260	0.110	0.115	0.173	0.100	0.003	0.064	0.210	0.080
MgO	0.020	0.020	0.023	0.020	0.010	0.020	0.010	0.010	0.020	0.020	0.020	0.010	0.005	0.000	0.020	0.040
Na2O	0.085	0.163	0.128	0.143	0.135	0.130	0.075	0.118	0.105	0.133	0.105	0.150	0.078	0.104	0.140	0.110
Li2O	7.170	7.260	7.980	7.440	7.210	7.290	7.460	7.310	7.390	7.500	7.510	7.210	7.250	7.450	6.630	7.550
Total	99.230	99.818	100.418	101.468	98.838	99.345	99.610	99.470	99.548	99.993	101.435	100.548	99.385	99.946	99.995	100.188
wt % cations																
Si	30.270	30.136	29.983	30.200	30.080	30.160	29.983	30.336	30.087	30.035	30.197	30.362	30.263	30.315	30.494	30.300
Al	14.700	14.212	13.847	14.278	14.782	13.951	14.683	14.345	14.665	14.713	14.432	14.265	14.712	14.072	14.140	14.334
Fe3+	0.042	0.716	0.944	0.432	0.180	1.070	0.325	0.181	0.187	0.012	0.234	0.480	0.011	0.602	0.334	0.220
Mn	0.031	0.161	0.183	0.086	0.065	0.101	0.068	0.202	0.086	0.089	0.132	0.077	0.002	0.042	0.163	0.062
Mg	0.012	0.012	0.014	0.012	0.006	0.012	0.006	0.006	0.012	0.012	0.012	0.006	0.003	0.000	0.012	0.024
Na	0.064	0.121	0.094	0.105	0.101	0.097	0.066	0.088	0.078	0.098	0.077	0.111	0.069	0.077	0.104	0.081
Li	3.388	3.378	3.661	3.405	3.388	3.409	3.479	3.414	3.434	3.558	3.485	3.331	3.388	3.462	3.080	3.500
# of cations																
Si	2.000	2.013	1.998	2.015	1.997	2.012	1.993	2.016	1.990	1.994	2.007	2.020	2.000	2.017	2.028	2.013
T site	2.000	2.013	1.998	2.015	1.997	2.012	1.993	2.016	1.990	1.994	2.007	2.020	2.000	2.017	2.029	2.013
Al	1.016	0.988	0.982	0.989	1.023	0.999	1.016	0.993	1.017	1.017	0.999	0.987	1.016	0.975	1.000	0.991
Fe 3+	0.002	0.024	0.032	0.015	0.006	0.036	0.011	0.006	0.006	0.000	0.008	0.016	0.000	0.022	0.011	0.008
M1 site	1.018	1.012	0.994	1.004	1.029	1.005	1.027	0.990	1.022	1.017	1.009	1.003	1.016	0.997	1.011	0.999
Mn	0.001	0.005	0.007	0.003	0.002	0.004	0.002	0.007	0.003	0.003	0.004	0.003	0.000	0.001	0.006	0.002
Mg	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.001	0.002
Na	0.005	0.010	0.008	0.009	0.008	0.008	0.005	0.007	0.007	0.008	0.008	0.009	0.005	0.006	0.009	0.006
Li	0.901	0.893	0.997	0.917	0.911	0.921	0.936	0.918	0.924	0.956	0.937	0.907	0.910	0.932	0.930	0.941
M2 site	0.908	0.900	1.012	0.930	0.922	0.933	0.943	0.933	0.934	0.968	0.949	0.908	0.915	0.940	0.945	0.951

Figure 27: Colour of spodumene crystals in relation to Mn, Fe and Na content of the mineral.

Figure 28 (a) through (f): Variations of the δLi (‰) with bulk composition of Spodumene crystals.

Figure 29: $\delta^6\text{Li}$ (‰) as a function of (a) wt % Li, and (b) the ratio of Li to the other M2 site occupants, of Spodumene crystals.

In Figure 28 (a) through (f), $\delta^6\text{Li}$ values are plotted as a function of specific bulk chemical components of the spodumenes. Apparent trends in correlation are indicated with dotted lines. In general, $\delta^6\text{Li}$ values become less negative (i.e., lighter) with increasing Si (Figure 28a), Fe (Figure 28e), Na (Figure 28c) and Mn (Figure 28f). No apparent correlation was observed between lithium isotope ratios and Mg content of spodumenes (Figure 28d). Finally, $\delta^6\text{Li}$ values become less negative (i.e., lighter) with decreasing Al (Figure 28b), and wt % Li (Figure 29a). The most obvious correlations are observed between the Mn content of spodumene (Figure 28f) and its $\delta^6\text{Li}$ value, and between the ratio of Li to other M2 site occupants (Figure 29b) and the $\delta^6\text{Li}$. From the information in these graphs there is a definite indication of bulk compositional control over the Li isotope composition of the various samples of spodumene.

The sample FB.G2 is unique in this data-set, in that the spodumene measured was of a secondary origin; that is, the spodumene crystal had an origin other than magmatic crystallization. Furthermore, it has a chemical composition that is near "pure" spodumene (Table 14), although the lithium content is lower than ideal. In Figure 27 (d,e, and f) it does not plot within the boundaries which outline the trends followed by the other spodumenes (see arrows). Its $\delta^6\text{Li}$ value is -6.8 ‰ which is much heavier than the other Georgia lake sample measured of -2.6 ‰. Although this is only one sample, it would seem to indicate that the isotopic composition of a secondary mineral is heavier than that of a corresponding primary mineral within the same pegmatite. This is quite a predictable

scenario, considering the fact that within pegmatites, secondary minerals are often a result of auto-metasomatism. The consequence of auto-metasomatism, is that the fluids from which the lithium in FB.G2 was derived are late-stage fluids derived from the same magma that crystallized the pegmatite. The literature seems to indicate that ^7Li preferentially prefers solvation, and therefore, will partition more strongly into the exsolving fluid phase. In addition, the lighter isotope of lithium is expected to have a higher binding energy in a covalent bond (Karplus and Porter, 1970), and therefore, once crystallized, becomes less mobile. The final result, is that late stage metasomatizing fluids are enriched in ^7Li , relative to minerals already crystallized. This explains the situation observed between FB.G1 and FB.G2.

6.5 COEXISTING MINERAL PAIRS

In this section, the lithium isotope composition of coexisting mineral phases have been determined. This is a particularly interesting type of study from the point of view of stable isotope geothermometry. As of yet, Li-isotopes have not been used in this regard, largely because of the difficulty of obtaining precise Li-isotope ratios, and because of lack of experimental data on the temperature dependance of Li-fractionation. Table 15 summarizes the determined lithium isotopic compositions of the coexisting phases of lepidolite and elbaite ($\pm$ cookeite), and amblygonite/eosphorite.

The first thing to note in Table 15, is that all coexisting phases have measurable

Table 15 - Lithium Isotope Analyses of Coexisting Mineral Pairs

Sample Number	Mineral Name	Measured $\delta^6\text{Li}$ (‰) ¹	Δ i-j (‰) ²	(i-j)
39403 A	Amblygonite	-5.7		
39403 B	Eosphorite	0.7	-6.4	A-B
43159A	Elbaite	-7.7	+3.2	A-B
43159B	Cookeite	-10.9	-7.0	B-C
43159C	Lepidolite	-3.9	-3.8	A-C
F90-15A	Lepidolite	-6.6		
F90-15C	Elbaite	-10.3	-3.7	C-A
50914A	Elbaite	-11.3		
50914B	Lepidolite	-13.2	+1.9	A-B
43182A	Lepidolite	+1.1		
43182B	Elbaite	-4.1	-5.2	B-A

¹ $\delta^6\text{Li}$ is calculated relative to the standards IRM-016.

² Δ i-j for a mineral pair is calculated using the formula: Δ i-j = $\delta^6\text{Li}_i - \delta^6\text{Li}_j$, and represents the relative fractionation ^6Li between mineral i and mineral j.

differences in isotopic composition [i.e., $\Delta(i-j)$]. This indicates that Li-isotopic compositions are not homogeneous between the phases (as would be expected at very high temperatures of isotopic equilibration). Second, $\Delta(i-j)$ is somewhat larger when one of the phases is an alteration product. For example cookeite-lepidolite = -7.0 ‰; amblygonite-eosphorite = -6.4 ‰, as compared to elbaite-lepidolite pairs which are < -5.2 ‰. This is an expected result of low temperature equilibration of isotopes. Finally, when comparing only a specific mineral pair (e.g., elbaite-lepidolite), pairs from different localities possess different $\Delta(i-j)$ values, while pairs from the same localities (F90-15 and 43159 are both from Mount Mica, Maine) have similar values (see Table 15). This is consistent with each pair crystallizing at a different temperature (likely ≤ 600 °C) depending on its origin, since if they all crystallized at roughly the same temperature, it would be expected that $\Delta(i-j)$ values would also be similar. These observations are encouraging to the notion that lithium isotope ratios may be successfully used in stable isotope geothermometry applications with future work.

6.6 SUMMARY AND DISCUSSION

The foregoing chapter has uncovered some interesting information. Firstly that lithium isotope geochemistry is controlled by both crystallographic and bulk chemical composition of a mineral. Secondly, the data for the triphyllite-lithiophilite-amblygonite series indicates that isotopic composition is variable with position in the crystallization sequence. The range of $\delta^6\text{Li}$ values observed for triphyllite, the Fe end-member of the

triphyllite-lithiophilite series, does not overlap with that of the lithiophilite range (see Figure 20). Furthermore the earlier crystallization product, triphyllite, has a much lighter isotopic composition than both lithiophilite and amblygonite. This is consistent with magma becoming preferentially enriched in ^7Li with progressive crystallization.

Further understanding of the isotope geochemistry of lithium is revealed by the study of the two spodumene samples FB.G1 (primary origin) and FB.G2 (secondary origin) from the Georgia Lake Field. The spodumene of metasomatic origin has a noticeably heavier isotopic composition than the primary magmatic spodumene (i.e., -6.8 and -2.6 ‰ respectively). The indication being that ^7Li preferentially partitions into late-fluid phases within pegmatites, and that ^6Li preferentially partitions into earlier crystal phases. In general, then, the evidence seems to overwhelmingly support the unequal partitioning of ^6Li and ^7Li between crystal and fluid phases, with ^7Li preferentially partitioning into the fluid phase. This hypothesis would also be supported by the $\delta^6\text{Li}$ value measured for lithiophorite. Lithiophorite is formed by chemical precipitation of Li from aqueous solution at low temperatures, and has the most positive $\delta^6\text{Li}$ value measured in this study (+3.5 ‰).

In addition, this study has revealed that spodumenes which crystallized from peraluminous magmas have lighter isotopic compositions than spodumenes that crystallized from metaluminous magmas. The Fairservice/Gullwing Lake pegmatites are identified as peraluminous (Breaks and Janes, 1991), and the ratios obtained for these

samples (FB.D1, FB.D2, FB.D3, FB.D4) are: -3.4, -8.1, -3.0, and -3.9 ‰ respectively. The Tot Lake pegmatites, on the other hand, are metaluminous in composition (Breaks and Janes, 1991), and the ratios obtained for these samples (FB.D5, FB.D6, FB.D7, FB.D8) are: -12.3, -12.2, -12.7 and -10.2 respectively. The results coincide with the findings in Chapter 7, that micas from peraluminous magmas have lighter isotopic compositions than micas from metaluminous (Figure 30).

Finally, studies of coexisting mineral pairs seem to indicate that these minerals crystallize at temperatures below that of Li-isotope homogenization. Because of this, Li-isotopes, may potentially be used in stable isotope geothermometry if there is any future development in experimentally determined data for Li-fractionation temperature dependence in the literature.

CHAPTER 7

LITHIUM ISOTOPE STUDY OF TOPAZ GRANITES

7.1 INTRODUCTION

As an example of how lithium isotopes may be applied to an actual petrological and geochemical study, lithium isotope ratios have been measured for mica separates from topaz granites from three locations: the Pleasant Ridge pluton in southern New Brunswick, the Vakkara granite phase of the Eurajoki pluton, Eurajoki, Finland, and the NMLG (non-megacrystic lithian mica granite) of the St. Austell pluton from St. Austell, England. These granites have recently been studied by Taylor, 1992. Lithium isotope ratios were measured on mineral separates of the main lithium-bearing phase in each granite: zinnwaldite (Pleasant Ridge pluton), lithian-siderophyllite (Eurajoki pluton), and lepidolite (St. Austell pluton), and have been compared to oxygen and hydrogen isotope values for corresponding whole rock samples (performed by Taylor, 1992).

7.2 GENERAL GEOLOGY

Taylor 1992 reports that the Pleasant Ridge pluton at Bonny River in southern New Brunswick, part of the Pomeroy Intrusive Suite, was emplaced around 360 Ma

(Late Devonian) into Lower Paleozoic rocks. The granite is post-tectonic (Acadian), epizonal to mesozonal in character and is of interest primarily because of its proximity to the Sn, Mo and W mineral deposits of Mount Pleasant. The Pleasant Ridge and Bonny River plutons are considered to be the first reported occurrences of topaz granite in the northern Appalachians. The Eurajoki, Finland topaz granite is mid-Proterozoic (ca. 1570 Ma), and the St. Austell granite is Phanerozoic [Pennsylvanian/Early Permian (ca. 280 Ma)].

7.3 PETROLOGY

Taylor, 1992 reports that granite from the Pleasant Ridge pluton is a fine- to medium-grained, alkali-feldspar granite, equigranular to seriate textures, with essential quartz, alkali feldspar, plagioclase, lithian mica and topaz. Accessory minerals include zircon, Nb-rutile, columbite-tantalite, cassiterite, uraninite, monazite and bastnasite. The granites contain primary albite ($An_{0.3}$) and are subsolvus in type. The lithian-micas of Pleasant Ridge occur as interstitial subhedral grains with inclusions of accessory minerals, however, mica inclusions are typically observed in quartz and K-feldspar, as well as interstitial to the quartz and feldspar, thus constraining their crystallization history. Pleasant Ridge Li -micas have been classified as zinnwaldite, with the main mechanism of substitution being cited as ${}^{\text{VI}}\text{Li} + {}^{\text{IV}}\text{Si} = {}^{\text{VI}}\text{Fe}^{2+} + {}^{\text{IV}}\text{Al}$ (Henderson et al., 1989, Fe-bearing lithian mica series).

Plagioclase of the Eurajoki Vakkara Granite also has $An_{0.5}$ (Haapala, 1977), and St. Austell pluton has An_2 (Manning and Hill 1990). The St. Austell pluton (non megacrystic lithian mica granite) unit is a medium to fine-grained rock characterized by the presence of essential euhedral to subhedral topaz in addition to lithian mica of the series zinnwaldite-lepidolite, albite, orthoclase, and quartz (Manning and Hill, 1990). Zinnwaldite is found as euhedral inclusion in quartz and K-feldspar grains which do not show any indication of strain, and apatite and amblygonite-montebrazite are present as accessory minerals not present in the other two granites.

The Vakkara granite phase of the Eurajoki pluton contains zircon, cassiterite, bastnasite and monazite as common accessory minerals as well as Nb-rutile columbite, thorium-xenotime, magnetite and ilmenite as well as molybdenite as sparse accessories (Haapala, 1977). All of the granites have essential quartz, K-feldspar, albite ($An_{0.5}$), F-rich topaz, lithian mica, and some common accessory minerals.

7.4 GEOCHEMISTRY

Both the topaz and Li-mica of the Pleasant Ridge pluton were found to be F-rich (17.6-19.4; and 5.9-7.4 wt % respectively). Taylor 1992 reported the wt % Li of the lithian mica to be 1.32 wt % measured by atomic absorption spectroscopy and the variety to be zinnwaldite. ICP-MS measurements of this study found wt % Li of the zinnwaldite to be 1.47 wt %. The difference is best explained by inhomogeneity of Li content between

the small sample sizes measured.

Pleasant Ridge granites are weakly peraluminous ($A/CNK = 1.02-1.12$) with high $SiO_2 > 75\%$, Li from 703-1124ppm, F $> 0.69\%$, elevated MnO $> (0.07-0.09\text{ wt } \%)$, as well as elevated Rb, Y, Sn, Cs, Ta, W and U. TiO_2 is depleted in wt % as are MgO, CaO, and P_2O_5 . This particular pluton is found to have a distinctive lower P_2O_5 content than the other two plutons ($< 0.1\text{ wt } \%$) and $Al_2O_3 < 14.5\%$ with a higher $SiO_2 (> 73\text{ wt } \%)$. It also has a higher abundance of REE, Y, and Th, and has been characterized as a "low-P" subtype of topaz granite. The Mn content results from the Mn-rich nature of the Li-mica present, and unlike many common granite types, Na_2O is greater than K_2O with molar ratios Na/K 1.42-1.63. Furthermore, the total Fe is low compared to other types of granite. The Eurajoki pluton is also characterized as a "low P" granite, while the St. Austell pluton may be termed "high-P" ($P_2O_5 > 0.4\text{ wt } \%$, $Al_2O_3 > 14.5\text{ wt } \%$, $SiO_2 < 73\%$ very low REE, Y and Th).

7.5 ISOTOPE GEOCHEMISTRY

Taylor 1992 reported that $\delta^{18}O$ values are nearly constant for the Pleasant Ridge Granites 8.1-8.6 ‰, whereas δD values have a broad range from -66 to -106 ‰, relative to SMOW, Standard Mean Ocean Water reference Standard. The δD values were interpreted to be indicative of magmatic degassing which was assumed to have occurred during emplacement. $\delta^{18}O$ values for the St. Austell and Eurajoki plutons are

also both fairly uniform for each pluton, but both Eurajoki and Pleasant Ridge compositions are heavier than the St. Austell values.

Results of oxygen and hydrogen isotope whole rock analyses from Taylor 1992 and lithium isotope analyses from this study are shown in Table 16, and in Figures 30 and 31. Lithium isotope ratios for micas correlate nicely with oxygen isotope ratios for whole rock determinations. Interestingly, as the oxygen composition of the whole rock gets heavier, the lithium composition of the mineral gets lighter. This may be analogous to the already discovered facts, that Li-isotope fractionations vary inversely with K, Rb (Oi et al., 1991), or Sr (Plyusnin et al., 1978) fractionations under the same conditions.

The Pleasant Ridge topaz granite is consistent with an I-type granite (Taylor, 1992). Eurajoki is also I-type and is metaluminous in character. On the other hand, St. Austell is consistent with a source which has an important component of pelitic sedimentary material (Miller 1985), which is supported by its more strongly peraluminous character. Fawwarah Saudi Arabia samples (181800-181904) (Dubray 1984) and Zinnwald, Czechoslovakia (46801) (Stemprok and Sylcek, 1969, Tischendorf and Forster 1990) are derived from "low P", I-type granites, and have comparatively heavier isotopic compositions (see Table 12), than the St. Austell S-type granite.

The enrichment of S-type granites in ^{18}O is interpreted to be a result of the enrichment of ^{18}O sediments during processes of surface weathering (Taylor 1968, Saving

Table 16: Lithium, Oxygen and Hydrogen Isotope Analysis of Topaz Granites

Sample Number	Locality ¹	<u>Whole Rock</u> ²		<u>Single Mineral</u> ³	Mineral Name
		$\delta^{18}\text{O}$ (‰)	δD (‰)	$\delta^6\text{Li}$ (‰)	
82-5	Pleasant Ridge Pluton	8.2	-72	-4.5	zinnwaldite
2273	St. Austell Pluton	10.6	-44	-2.0	lepidolite
1160	St. Austell Pluton	11.1	-74	-1.7	lepidolite
1091	St. Austell Pluton	11.8	-100	-0.5	lepidolite
149/70	Eurajoki, Finland	9.6	-70	-3.2	li-siderophyllite

¹See Taylor 1992 for information on localities.

²Values from Taylor 1992 relative to SMOW (Standard Mean Ocean Water)

³Values relative to IRM-016.

Figure 30: Plot of $\delta^6\text{Li}$ for Li-micas versus whole-rock $\delta^{18}\text{O}$ from three topaz granites. Locations and sample numbers are noted on the graph.

Figure 31: $\delta^6 Li$ (‰) for Li-micas versus whole-rock δD from three topaz granites. Locations and sample numbers are noted on the graph.

& Epstein 1970). Conversely, the enrichment of lithium isotopes in ^6Li in S-type granites may be a result of leaching of the ^7Li during the same processes of surface weathering. The literature seems to support the case that ^7Li preferentially favours solvation (i.e., St. Austell Pluton).

While the strongly negative δD values (up to -100‰) supported the theory of magmatic degassing during ascent and emplacement (c.f., Nabelek et al., 1983), the apparent lack of correlation between lithium isotope ratios (Figure 31) and hydrogen isotope ratios indicates that degassing is not a major control for lithium isotope fractionation, for the conditions under which the Pleasant Ridge and St. Austell pluton were emplaced. This may, in large part, be due to the fact that the Li-micas may have already crystallized as an early phase, prior to exsolution of the aqueous fluid (Taylor, 1992), and remain fairly intact during the degassing. If this is in fact the case, Li-isotope studies of Li-micas (which occur in various generations during the emplacement of pegmatites, in particular (Hawthorne and Cerny, 1982)) may be used to constrain the timing of the exsolution of the aqueous phase (i.e., degassing). Similarly, magmatic degassing has only a minor influence of oxygen isotope fractionation in these same magmas (Taylor, 1992).

7.6 CONCLUSIONS

1. $\delta^6\text{Li}$ values correlate with $\delta^{18}\text{O}$ values for micas from topaz rhyolites in a linear

fashion.

2. Lithium isotopic composition gets lighter as oxygen isotopic composition gets heavier.
3. S-type peraluminous, high-P granites have light $\delta^6\text{Li}$ values.
4. I-type metaluminous, low-P granites have heavier $\delta^6\text{Li}$ values.
5. Surface weathering should result in the isotopic composition of the residual minerals becoming lighter, while secondary minerals should have heavier compositions.
6. Li-isotope studies may be useful in timing fluid exsolution in pegmatite emplacement.

CHAPTER 8

CONCLUSIONS

8.1 DISCUSSION

The objectives of this study were to develop a method whereby reliable and precise lithium isotope ratios could be determined using Inductively Coupled Plasma Mass Spectrometry, and then to employ this method to measure natural mineral samples. Four such suites of samples were measured: a) a suite of Li-bearing minerals of varied chemistry, b) a suite of spodumene samples, c) a suite of micas from topaz granites, and d) a suite of coexisting mineral pairs. For each suite, it was hoped that certain information concerning the isotopic geochemistry of lithium could be elucidated. In general, the endeavour of the individual studies were to a) obtain an approximation of the range of lithium isotope ratios found in natural crustal samples, b) determine if any relationship exists between lithium isotopic composition of minerals and their bulk chemical composition, c) determine to what extent, if any, magmatic degassing affected the lithium isotope ratios in topaz granites, d) determine if lithium isotope ratios partition between coexisting mineral phases, and e) determine if any generalities concerning the isotopic systematics of lithium could be deduced from the data obtained in the study.

This study has made a significant contribution to the current state of knowledge concerning the lithium isotope geochemistry of crustal minerals. A method was developed

in Part I, capable of determining lithium isotope ratios on samples of lithium minerals <10 mg, at concentrations ~60 ppb, with an estimated precision of 0.8 ‰. In Part II, evidence was gathered concerning a bulk chemical control of lithium isotope ratios in spodumenes, as well as a crystallographic control over lithium isotopic composition in different minerals. The range of $\delta^6\text{Li}$ (relative to IRM) values found was -33.2 ‰ to + 3.5 ‰ for all the minerals measured, with the interesting observation that low temperature, primary or alteration minerals had positive $\delta^6\text{Li}$ values, while primary magmatic minerals had heavier compositions. In fact, in a comparison between a pair of spodumenes from the same pegmatite, one primary, and one derived from secondary metasomatic fluids, the later-generation spodumene had a more negative $\delta^6\text{Li}$ value than the primary one. This suggestion of increased ^7Li enrichment with increasing magma fractionation, was also indicated, to a degree, by the isotope values obtained for the samples from the lithiophilite-triphyllite series. Triphyllite, the earlier crystallizing Fe end-member, had a much lighter isotopic composition than the more evolved Mn end-member, lithiophilite. Furthermore, the $\delta^6\text{Li}$ ranges for the two species did not overlap.

A study of mica separates from topaz granites revealed that Li isotope ratios were not affected by magmatic degassing processes to the same degree as hydrogen isotopes, however, the study of the micas revealed that Li-micas from S-type granites had lighter isotopic compositions than those from I-type granites. The isotopic composition of spodumenes also seemed to be affected by the peraluminosity, with peraluminous pegmatites having lighter isotopic compositions than pegmatites that crystallized from

metaluminous magmas. This is the opposite trend to what is observed for ^{18}O isotopes. In fact, a plot of $\delta^{18}\text{O}$ versus $\delta^6\text{Li}$ for the topaz granites (Figure 30) showed an inverse relationship between the behaviour of lithium isotope ratios and oxygen isotope ratios. Inverse relationships between Li-isotope fractionations and K, Rb (Oi et al., 1991), and Sr (Plyusnin, 1978) have already been reported in the literature.

Although, in some cases, only a few minerals of a given category were analyzed, the following list summarizes the indications of the data obtained in this study, and the data available in the current literature, with respect to lithium isotope systematics.

Enriched in ^6Li (values shown are $\delta^6\text{Li}$ ‰)

1. Low T minerals (i.e., authigenic/clay minerals, meteoric alteration minerals, Mn-deposits). (This Study, Chan et al., 1992)

Hectorite (clay)	+1.7
Eosphorite (on amblygonite)	+0.7
Lithiophorite (Mn-deposit)	+3.5
2. Minerals depleted in total Li as a result of metamorphism. (Chan et al., 1992)

Metamorphosed basalt	+2.1
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3. Minerals precipitated early in fractional crystallization. (This Study)

Triphyllite vs. Lithiophilite	(-0.3 to -2.7 vs. -4.8 to -9.5)
Primary Spodumene vs. Secondary Spodumene	(-2.6 vs. -6.8)
4. Chemical precipitates. (Cameron, 1955)
5. S-type granites (variable depending on mineral measured) (This Study)

Enriched in ^7Li (values shown are $\delta^6\text{Li}$ ‰)

1.	Mantle derived minerals.	(Chan and Edmond, 1988)
	Fresh MORB Basalt	-4.7 to -6.3
2.	Primary igneous minerals (variable).	(This Study)
3.	Minerals derived from a metasomatic fluid of a magmatic source (as above for spodumene pair).	(This Study)
4.	Waters	(Chan et al., 1992)
	Ocean	-32.3
	Fresh Water	-15.3 to -18.5
	Ridge Hydrothermal Fluids	-5.5 to -11.8

In addition, when comparing the relationships between lithium content of mineral types and $\delta^6\text{Li}$ values, it was noticed that both primary and alteration minerals had a trend of decreasing lithium content corresponding to lighter isotopic compositions. The exceptions to this rule were the two minerals tourmaline and holmquistite. Both of these minerals form in the exomorphic halos of Li-rich pegmatites, and are the result of wall-rock metasomatism by the intruding pegmatite. Both of these minerals had definite trends of increasing lithium concentration as isotopic composition became lighter. This is perhaps indicative of the preferential partitioning of ^7Li into the fluid phase during metasomatism (i.e., the earliest crystallized exomorphic minerals will have the highest Li contents but the lightest isotopic composition, and minerals become isotopically heavier outwards from the intrusion as Li-content decreases).

8.2 CONCLUSIONS

1. Lithium isotope ratios can be determined by ICP-MS with a precision in the order of 0.8 ‰.
2. Crustal minerals have a range of lithium isotopic composition on the order of - 33.2 ‰ to + 3.5 ‰.
3. Mineral species from peraluminous host rocks will have a lighter isotopic composition than the same mineral species from a metaluminous equivalent host rock.
4. Lithium isotope ratios vary inversely with oxygen isotope ratios.
5. Low temperature minerals have lighter isotopic compositions than primary magmatic minerals.
6. Isotopic composition of minerals becomes heavier with increased magmatic evolution.
7. Late stage fluids in pegmatites are enriched in ^7Li .
8. Exomorphic Li minerals become isotopically heavier as Li content decreases.

8.3 IDEAS FOR FUTURE RESEARCH

Further research into the area of lithium isotopes may take two primary directions. In the direction of methodology, there is work to be done with the possibility of matrix modification (possibly with Na) for improving the stability of isotope ratio measurements,

and on the improvement of lithium separation techniques so that faster sample throughput and more difficult separations can be achieved.

In the area of lithium isotope applications in geoscience, mineral pairs studies gave evidence that there may be potential in pursuing the study of lithium isotope geothermometry. Moreover, lithium may also be very useful in fluid evolution studies of pegmatites.

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APPENDICES

APPENDIX I - STATISTICAL FORMULAE AND METHOD OF DATA REDUCTION FOR ISOTOPE RATIO DETERMINATIONS

Measurement Protocol

According to the general measurement protocol, *blocks* of five consecutive apparent ratios are collected for each of the following solutions in the order, blank-standard-sample-standard-blank, comprising one sample 'run'. During actual measurements however, blocks of six consecutive ratios were occasionally collected in order to increase precision, while at other times, blocks of 4 or less measurements were collected due to time constraints in the analytical session. Using fewer consecutive measurements decreases the precision with which ratios can be determined. In addition, when the background signal was low relative to the analyte signal, it was often found to be sufficient to measure blanks at intervals of approximately two hours, rather than after each sample 'run'.

Data Reduction

The method of data reduction described below was applied consistently to all lithium isotope data collected in this study. The following steps were taken in order to compile the data.

1. For each *apparent ratio* collected in the block of measurements, a time-weighted average of the closest blank value determined before, and the closest blank value determined after each ratio is subtracted from the measurement, giving a *net apparent isotope ratio*.
2. A Q-test is then performed on each *net apparent ratio* within the block using the 90% confidence interval, where Q is given by:

$$Q = \frac{a}{w}$$

where, w is the range from highest to lowest ratio in the block,
and, a is the range from the suspected outlier to the next closest data point.

3. All data that fails the Q-test for blocks with $n > 3$ determinations is rejected. Data may also be rejected based on known experimental error or deficiencies.
- 4a). In most cases, the remaining values are averaged to obtain the *average net*

apparent ratio. The average net apparent ratio is associated with the uncertainty S_n .

$$\bar{X} = \frac{1}{\sum RSD_i^{-2}} \left(\sum \frac{X_i}{RSD_i^2} \right)$$

where, S_n represents the best estimate precision for the ratio (also known as the standard error of the mean),

n is the number of unrejected measurements in the block,

and, s_n is the sample standard deviation for the block of measurements. The sample standard deviation, s_n , is given by:

$$s_n = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

where, x_i is an individual measurement in the block,
and, $\bar{x}$ is the average net apparent isotope ratio.

- 4b). In some cases, a weighted mean (using the RSD reported by the ELAN software for each individual determination as the weighting factor), rather than an average, must be calculated to obtain the average net apparent isotope ratio. This is necessary when sporadic instrumental fluctuations affect measurements such that the RSDs reported by the ELAN software for each individual determination within a block are highly variable. The weighted mean, $\bar{x}$, is given by:

$$\bar{x} = \frac{1}{\sum RSD_i^{-2}} \left(\sum \frac{x_i}{RSD_i^2} \right)$$

where, x_i is an individual measurement,

and, RSD_i is the RSD for the individual measurement, reported by the ELAN software.

The uncertainty associated with this mean is the same as that given in 4a).

5. An average correction factor is calculated for the standard solutions bracketing the

sample block. The average net apparent isotope ratio is multiplied by the correction factor to obtain the *net corrected ratio*. When an average correction factor is applied, the uncertainty associated with the net corrected ratio is given by:

$$S_{Cratio} = Cratio \times \sqrt{\left(\frac{S_{ratio}}{ratio}\right)^2 + \left(\frac{S_{cf}}{Cf}\right)^2}$$

where, *Cratio* is the net corrected ratio,
ratio is the average net apparent ratio,
Cf, is the correction factor,
 and, $S_{ratio} = S_n$ for the block
 and,

$$\frac{S_{cf}}{Cf} = \frac{1}{\bar{X}_{std}} \times \sqrt{\left(\frac{s_{std_1}}{\sqrt{n}}\right)^2 + \left(\frac{s_{std_2}}{\sqrt{n}}\right)^2}$$

Note: if sudden instrument shifts were noticed between sample "runs" rather than gradual instrumental drift, only the standard run after the shift was used to calculate the correction factor.

The values reported in Appendix IV are the *net corrected ratio* $\pm S_{Cratio}$, for each block of consecutive sample measurements.

6. In many cases, more than one 'run' was performed for a particular sample. When a sample was remeasured, each net corrected ratio was treated as an individual *replicate*, and the best estimate of precision for the mean of all replicates for the same sample, is given by:

$$S_{samp} = \frac{s_{samp}}{\sqrt{n}}$$

where, *n* is the number of replicates,
 and, s_{samp} is the sample standard deviation between the replicates.

The values reported in Table 12 represent the mean of all replicates for each particular sample and its associated uncertainty.

Even though some blocks of measurements (i.e. average net apparent ratio) appear to have large standard deviations, comparison of replicate groups consistently gives an indication of better precision. The fact that single blocks show larger variation can often be due to "noisy" signals (i.e. short-term stability). A "noisier" signal, however, will still produce a mean, albeit with a larger standard deviation within the group of measurements, that has the same degree of reproducibility from one replicate of the experiment to the next. i.e. even replicates performed on different days under different instrument conditions still yield results with the same degree of reproducibility. For this reason, the precision of the method is independent of the standard deviation of a single group of measurements for a sample, this is largely only dependent on instrument noise.

APPENDIX II - SAMPLE LOCALITIES AND DESCRIPTIONS

Sample Number	Donor	Mineral Name	Locality	Location	Host Rock	Description
82-5	RPT	Zinnwaldite	Pleasant Ridge, New Brunswick	Pleasant Ridge Pluton	Topaz Granite	Mineral separate: brown, subhedral fine-grained, 1-2mm flakes.
1091	RPT	Lepidolite	St. Austell, England	St. Austell Pluton	Topaz Granite	Mineral separate: light pink, subhedral, fine-grained, 1-2mm flakes.
1160	RPT	Lepidolite	St. Austell, England	St. Austell Pluton	Topaz Granite	Mineral separate: light pink, subhedral, fine-grained, 1-2mm flakes.
149-70	RPT	Siderophyllite	Eurajoki, Finland	Eurajoki Pluton	Topaz Granite	Mineral separate: dark brown, subhedral, fine-grained, 1-2mm flakes.
181800	RPT	Li-mica	Fawwarah, Saudi Arabia	—	Topaz Granite	Mineral separate: brown, subhedral, fine-grained, 1-2mm flakes.
181878	RPT	Li-mica	Fawwarah, Saudi Arabia	—	Topaz Granite	Mineral separate: brown, subhedral, fine-grained, 1-2mm flakes.
181900	RPT	Li-mica	Fawwarah, Saudi Arabia	—	Topaz Granite	Mineral separate: brown, subhedral, fine-grained, 1-2mm flakes.
181904	RPT	Li-mica	Fawwarah, Saudi Arabia	—	Topaz Granite	Mineral separate: brown, subhedral, fine-grained, 1-2mm flakes.

Sample Number	Donor	Mineral Name	Locality	Location	Host Rock	Description
2273	RPT	Lepidolite	St. Austell, England	St. Austell Pluton	Topaz Granite	Mineral separate: light pink, subhedral, fine-grained, 1-2mm flakes.
301-PL	RPT	Siderophyllite	Eurajoki, Finland	Eurajoki Pluton	Topaz Granite	Mineral separate: dark brown, subhedral, fine-grained, 1-2mm flakes.
36660	CMN	Polybithionite	Mont St. Hilaire, Quebec	Pegmatite Dike	Nepheline Syenite	Monomineralic cluster of coarse-grained, euhedral amber coloured mica "books" ~5mm thick, 1cm across, arranged in rosettes. Heavily weathered appearance given by creamy beige colour and curling of individual mica plates along crystal edges.
38716	CMN	Triphylite	Newry, Maine	—	Granitic Pegmatite	Coarse, dark blue, anhedral crystal with vitreous lustre and no cleavage visible, in association with coarse-grained gold-coloured unidentified phyllosilicates.
38717	CMN	Triphylite	North Grooton, New Hampshire	Palermo Mine	Granitic Pegmatite	Coarse, grey-blue anhedral crystal with vitreous lustre, in association with vivianite. Micaceous alteration evident along cleavage.
38718	CMN	Lithiophilite	Bernic Lake, Manitoba	Tanco Mine	Granitic Pegmatite	Coarse, honey-brown anhedral crystal, with vitreous lustre and no cleavage visible in association with albite and quartz.
39403	CMN	Amblygonite/ Eosphorite	Minas Gerais, Brazil	—	Granitic Pegmatite	Large, euhedral, striated, greenish amblygonite crystal, 25cm x 15cm, with vitreous lustre, and esophorite present on weathered face, as a fine pink powder.
43159	CMN	Elbaite/ Cookeite/ Lepidolite	Mount Mica, Maine	—	Granitic Pegmatite	Radial elbaite, 2-3cm long, with colour zoning (cream → olive green → dark green), in association with massive coarse-grained, pink lepidolite. Dun brown cookeite, occurs interstitially to lepidolite flakes (on weathered face), and enveloping elbaite crystals.

Sample Number	Donor	Mineral Name	Locality	Location	Host Rock	Description
43172	CMN	Elbaite	Kenora, Ontario	Lily Pad Pound Occurrence	Granitic Pegmatite	Fractured, elbaite of the rubellite variety, occurs as crystals 4-5cm long in a feldspar matrix.
43182	CMN	Elbaite/ Lepidolite	San Diego County, California	--	Granitic Pegmatite	Fine elbaite needles (2mm x 2cm), of the rubellite variety, occur as rosettes in a matrix of very fine-grained, massive, light mauve lepidolite.
44757	CMN	Bixiaite	Kings Mountain, North Carolina	Footle Mine	Granitic Pegmatite	Fine-grained, white, granular texture.
45181	CMN	Holmquistite	Lac Malartic, Quebec	--	Granitic Pegmatite	Euhedral, purple-grey megacryst, displaying obvious ductile deformation.
46801	CMN	Zinnwaldite	Zinnwald, Czech Republic	--	Topaz Granite	Blackish-gold, anhedral, deformed mica (~10cm), cut by small grey, quartz-feldspathic veinlets (~1-2mm wide).
47726	CMN	Amblygonite	Bernic Lake, Manitoba	Tanco Mine	Granitic Pegmatite	Single white, opaque, euhedral, crystal (~10cm), displaying good cleavage in 2 directions, in association with quartz.
49684	CMN	Lithiophorite	Norman, Arkansas	North Mountain Mine	Mn-deposit	Black, reniform habit, with a fresh, unaltered appearance.
50597	CMN	Holmquistite	Brankovcen, Austria	--	Granitic Pegmatite	Acicular, purple-grey crystals, forming radial aggregates, in a sugary quartz matrix.
50914	CMN	Elbaite/ Lepidolite	Minas Gerais, Brazil	Aricanga Mine	Granitic Pegmatite	Highly fractured rubellite crystals (3cm x 0.5cm), in a matrix of medium grained (1-2mm) pink lepidolite. Weathered surface is gold to chalky yellow.
51429	CMN	Psalite	Karibib, Namibia	Rubicon Mine	Granitic Pegmatite	Single, large white crystal, translucent, with a vitreous lustre, and exhibiting one good cleavage and basal parting, with a fresh, unaltered appearance.
53407	CMN	Clinoholmquistite	Siberia, Russia	--	Granitic Pegmatite	Single, blue-grey, well cleaved, monoclinic crystal.

Sample Number	Donor	Mineral Name	Locality	Location	Host Rock	Description
54134	CMN	Lithiophilite	Rio Grande do Norte, Brazil	Caporia	Granitic Pegmatite	Resinous, amber-brown crystals (5-7cm), with no visible cleavage, and cores partially replaced with albite, occur in a matrix of albite.
ACL	RPT	Spodumene		Aclare Pegmatite	Granitic Pegmatite	Single, grey crystal (~15cm).
F86-59	JVV	Griocerite	Mont St. Hilaire, Quebec	Nepheline Syenite	Sodalite Inclusions	Fine, slightly yellowish, chalky, anhedral crystals (<1.5mm) occur in cores of villiamite crystals, in association with albite, argentine, eudialite, and some very rare accessory minerals.
F90-15	GR	Elbaite/ Lepidolite	Mount Mica, Maine		Granitic Pegmatite	Medium-grained crystals of the rubellite variety occur in a matrix of massive quartz, purple lepidolite (2-4mm), and cleavelandite.
FB.B1	FB	Spodumene	Beauregard Lake Field, Ontario	Pakigama Lake Pegmatite	Granitic Pegmatite	White, lath-like spodumene intergrown with grey quartz, and spatially closely associated with Li-Mn tourmaline (tsilasilite).
FB.C1	FB	Spodumene	Crescent Lake Field, Ontario	Tebishogishik Pegmatite No. 2	Granitic Pegmatite	Green spodumene associated with incipiently albitized blocky k-feldspar, green muscovite, smoky quartz and beryl.
FB.C2	FB	Spodumene	Crescent Lake Field, Ontario	Chappais Lake Pegmatite	Granitic Pegmatite	Green spodumene with minor micaceous alteration, associated with smoky quartz and local albite.
FB.D1	FB	Spodumene	Dryden Field, Ontario	Fairservice Pegmatite No. 1	Granitic Pegmatite	Light green spodumene associated with grey quartz and green muscovite.
FB.D2	FB	Spodumene	Dryden Field, Ontario	Fairservice Pegmatite No. 4	Granitic Pegmatite	Light green spodumene associated with grey quartz, green muscovite, albite and minor apatite.
FB.D3	FB	Spodumene	Dryden Field, Ontario	Fairservice Pegmatite No. 11	Granitic Pegmatite	Light green spodumene, associated with quartz, k-feldspar, albite, and tourmaline.
FB.D4	FB	Spodumene	Dryden Field, Ontario	Gullwing Lake Pegmatite	Granitic Pegmatite	White spodumene, locally altering to lepidolite along cleavages.

Sample Number	Donor	Mineral Name	Locality	Location	Host Rock	Description
FB.D5	FB	Spodumene	Dryden Field, Ontario	Tot Lake Pegmatite 91-1	Granitic Pegmatite	Light pink spodumene associated with albite, green muscovite and minor beryl.
FB.D6	FB	Spodumene	Dryden Field, Ontario	Tot Lake Pegmatite 91-2	Granitic Pegmatite	Light pink spodumene associated with albite, green muscovite and minor beryl.
FB.D7	FB	Spodumene	Dryden Field, Ontario	Tot Lake Pegmatite 91-3	Granitic Pegmatite	Pink, lath-like, spodumene associated with green quartz, fine-grained albite, green mica, spessartine and pollucite.
FB.D8	FB	Spodumene	Dryden Field, Ontario	Tot Lake Pegmatite 91-4	Granitic Pegmatite	Single, large pink spodumene megacryst.
FB.G1	FB	Spodumene	Georgia Lake Field, Ontario	Nama Creek Pegmatite	Granitic Pegmatite	Green, slender spodumene crystals oriented normal to dyke wall. Associated with albite, grey quartz, green muscovite and garnet, and altering to chlorite along cleavages.
FB.G2	FB	Spodumene	Georgia Lake Field, Ontario	MINW Pegmatite	Granitic Pegmatite	White, lath-like, secondary spodumene, formed via petalite breakdown.
FB.M1	FB	Spodumene	--	Ignace Pegmatite	Granitic Pegmatite	Green spodumene, with micaceous alteration along cleavages, associated with grey quartz, green muscovite and albite.
FB.M2	FB	Spodumene	King's Mountain, North Carolina	King's Mountain Pegmatite	Granitic Pegmatite	Green spodumene associated with k-feldspar, albite, apatite, green muscovite and smoky quartz.
FB.R1	FB	Spodumene	Root Lake Pegmatite Field, Ontario	Root Lake Pegmatite No. 1	Granitic Pegmatite	Faint brown spodumene associated with grey quartz, and minor k-feldspar, tourmaline and sericite.
FB.R2	FB	Spodumene	Root Lake Pegmatite Field, Ontario	Root Lake Pegmatite No. 2	Granitic Pegmatite	Faint brown to white spodumene associated with grey quartz, and minor albite, sericite, orange garnet and k-feldspar.
HECT	JCM	Hectorite	Yavapai County, Arizona	Lyles Mine	--	Massive, chalky white, very fine-grained.

APPENDIX II CONT'D**Donor Abbreviations**

RPT	-	Dr. Richard P. Taylor
CMN	-	Canadian Museum of Nature
JVV	-	Dr. Jerry Van Velthuisen
GR	-	George Robinson
FB	-	Dr. Fred Breaks
JCM	-	Dr. Juan-Carles Melgarejo

APPENDIX III - MINERAL DISSOLUTION PROCEDURE AND PLASTIC RESIN CLEANING PROCEDURE

Mineral Dissolution Procedure

- 1) Approximately 10-30 mg of each sample, powdered to 200 mesh with an agate mortar and pestle, was weighed on a Mettler AE100 analytical balance.
- 2) The samples were placed inside clean teflon screw cap vials (teflon cleaning procedure described below), and approximately 3 mL of concentrated Seastar HF was added.
- 3) The vials were then sealed and refluxed on a hot plate at 180 °C-190 °C for 12-18 hours. If, after this time, sample remained undissolved, ~1 mL more of concentrated Seastar HF was added and refluxing continued.
- 4) Concentrated Seastar HCL (~1 mL) was added to completely dissolved sample, or sample dissolved except for precipitate, to prevent the formation of CaF_2 during evaporation. Refluxing was continued for an additional 4-6 hours to redissolve any precipitate.
- 5) Solutions clear and free of precipitate, were taken to dryness at 90-120°C.
- 6) Sample residue was redissolved in 0.23N HCl or 0.12 N HCl in preparation for ion exchange.

Plastic Resin Cleaning Procedure

- 1) Teflon and plastics were washed by hand with Sparkleen™ detergent and distilled water.
- 2) Resins were then soaked in 50/50 v/v Anala R grade HNO₃ at 130 °C for ~ 2h.
- 3) Resins were then rinsed with distilled water and soaked in 50/50 v/v Anala R grade HCl at 130 °C for ~ 2h.
- 4) Resins were removed from HCl, rinsed in nanopure water, and soaked in nanopure water at 90 °C for ~ 2h, and at room temperature overnight.

APPENDIX IV

APPENDIX IV.1	-	ICP-MS DATA FOR SAMPLES PREPARED BY ION EXCHANGE
APPENDIX IV.2	-	ICP-MS DATA FOR SAMPLES PREPARED BY ACID-LEACHING
APPENDIX IV.3	-	ICP-MS DATA FOR REFERENCE MATERIALS

Abbreviations and Notations

ICP-MS	-	Inductively Coupled Plasma Mass Spectrometer
cps	-	ion counts per second
S	-	Standard Error (Best Estimate of Precision)
n	-	number of measurements in sample block

APPENDIX IV.1 - ICP-MS DATA FOR SAMPLES PREPARED BY ION EXCHANGE

Sample #	n	Net 7Li (cps)	Net 6Li (cps)	Correction Factor (1)	Corrected Ratio (2) ±	Standard Error (S.E.)	Delt 6Li vs. IRM-016 ± S.E
82-5	5	124,886	9,468.8	0.936213	12.348 ± 0.017	± 0.017	-4.7 ± 1.4
82-5	5	125,928	9,606.8	0.941765	12.345 ± 0.017	± 0.017	-4.5 ± 1.4
149-70	4	117,107	8,575.4	0.901840	12.316 ± 0.037	± 0.037	-2.1 ± 3.0
149-70	4	113,226	8,195.7	0.892482	12.330 ± 0.028	± 0.028	-3.2 ± 2.2
301-PL	4	114,331	8,262.5	0.889423	12.307 ± 0.024	± 0.024	-1.4 ± 1.9
1091	2	195,037	14,401.3	0.907970	12.297 ± 0.002	± 0.002	-0.5 ± 0.2
1160	3	128,676	10,137.6	0.969663	12.308 ± 0.014	± 0.014	-1.5 ± 1.1
1160-BLIND	3	122,371	9,638.6	0.969659	12.311 ± 0.013	± 0.013	-1.7 ± 1.1
2273	3	130,791	9,920.3	0.934081	12.315 ± 0.025	± 0.025	-2.0 ± 2.0
36660	4	241,696	12,876.9	0.860851	12.404 ± 0.039	± 0.039	-9.3 ± 3.2
38716	5	223,668	11,904.6	0.855095	12.308 ± 0.031	± 0.031	-1.5 ± 2.5
38716	5	223,677	11,895.2	0.855332	12.323 ± 0.036	± 0.036	-2.7 ± 2.9
38717	3	54,788	4,171.8	0.935911	12.291 ± 0.015	± 0.015	-0.1 ± 1.2
38717	4	53,975	4,109.3	0.936419	12.300 ± 0.016	± 0.016	-0.8 ± 1.3
38717-BLIND	4	54,021	4,110.4	0.935399	12.293 ± 0.013	± 0.013	-0.3 ± 1.1
38718	3	61,052	4,620.9	0.939039	12.407 ± 0.026	± 0.026	-9.5 ± 2.1
39403A	5	144,302	10,918.5	0.935234	12.360 ± 0.021	± 0.021	-5.7 ± 1.7
39403B	5	150,578	11,507.6	0.938620	12.282 ± 0.019	± 0.019	0.7 ± 1.6
43159A	4	119,963	8,628.0	0.890688	12.384 ± 0.027	± 0.027	-7.7 ± 2.2
43159B	2	119,657	8,582.8	0.891122	12.424 ± 0.019	± 0.019	-10.9 ± 1.5
43159C	4	71,220	5,405.7	0.936427	12.337 ± 0.017	± 0.017	-3.9 ± 1.4
43172	2	138,235	10,002.7	0.903513	12.486 ± 0.018	± 0.018	-16.0 ± 1.4
43172	5	224,332	11,855.3	0.660822	12.504 ± 0.021	± 0.021	-17.4 ± 1.7
43172	5	225,220	11,905.7	0.660898	12.502 ± 0.025	± 0.025	-17.3 ± 2.0
43182A	5	93,377	6,927.8	0.911126	12.281 ± 0.022	± 0.022	0.8 ± 1.8
43182A	5	116,303	8,449.2	0.891815	12.276 ± 0.025	± 0.025	1.1 ± 2.0
43182B	2	105,893	7,642.3	0.891817	12.357 ± 0.019	± 0.019	-5.5 ± 1.6

APPENDIX IV.1 CONT'D

Sample #	n	Net 7Li (cps)	Net 6Li (cps)	Correction Factor (f)	Corrected Ratio (Z)	Standard Error (S.E.)	Delt 6Li vs. IRM-016 ± S.E
43182B	5	104,518	7,537.6	0.890677	12.350	± 0.027	-4.9 ± 2.2
43182B	5	88,627	6,546.0	0.911492	12.341	± 0.025	-4.1 ± 2.1
44757	5	98,170	7,616.0	0.970289	12.507	± 0.006	-17.7 ± 0.5
R45181	4	251,065	13,470.3	0.660380	12.308	± 0.036	-1.5 ± 2.9
R45181	4	255,627	13,734.6	0.661069	12.304	± 0.036	-1.1 ± 2.9
46801	3	131,423	9,599.4	0.903519	12.370	± 0.025	-6.5 ± 2.0
47726	5	134,574	10,114.7	0.954386	12.698	± 0.021	-33.2 ± 1.7
49684	2	130,533	9,602.7	0.903515	12.282	± 0.044	0.7 ± 3.6
49684	5	202,778	10,949.2	0.661290	12.247	± 0.018	3.5 ± 1.4
49684	5	204,404	11,065.0	0.662969	12.247	± 0.019	3.5 ± 1.6
50597	5	246,287	13,059.0	0.659144	12.431	± 0.040	-11.5 ± 3.2
50914A	4	116,174	8,350.5	0.894134	12.439	± 0.024	-12.2 ± 1.9
50914A	5	98,935	7,255.8	0.911515	12.429	± 0.028	-11.3 ± 2.2
50914B	5	130,293	9,725.0	0.929427	12.452	± 0.031	-13.2 ± 2.5
51429	5	202,779	10,770.0	0.660292	12.432	± 0.035	-11.6 ± 2.8
53407	5	277,863	14,813.5	0.661919	12.416	± 0.045	-10.2 ± 3.6
54134	5	98,498	7,707.3	0.966287	12.349	± 0.010	-4.8 ± 0.8
181800	3	108,442	7,798.8	0.888103	12.349	± 0.011	-4.8 ± 0.9
181878	4	106,240	7,617.0	0.888524	12.393	± 0.019	-8.4 ± 1.6
181900	5	106,539	7,643.1	0.885560	12.344	± 0.022	-4.4 ± 1.8
181904	5	108,799	7,811.9	0.886603	12.348	± 0.019	-4.7 ± 1.6
ACL	4	134,693	10,019.0	0.915482	12.308	± 0.016	-1.4 ± 1.3
ACL	4	123,576	9,167.2	0.914285	12.325	± 0.017	-2.8 ± 1.4
CONTROL	4	132,234	10,423.3	0.969652	12.301	± 0.013	-0.9 ± 1.1
CONTROL	5	133,506	10,525.5	0.969658	12.299	± 0.014	-0.7 ± 1.1
F86-59	5	64,481	4,717.3	0.903661	12.352	± 0.030	-5.1 ± 2.4
F86-59	2	76,170	5,550.0	0.903979	12.407	± 0.022	-9.5 ± 1.8
F86-59	5	62,849	4,546.2	0.894543	12.367	± 0.028	-6.2 ± 2.3
F90-15A	3	73,324	5,335.2	0.898588	12.360	± 0.025	-4.9 ± 2.0
F90-15A	3	68,890	5,006.7	0.899052	12.371	± 0.048	-6.6 ± 3.9

APPENDIX IV.1 CONT'D

Sample #	n	Net 7Li (cps)	Net 6Li (cps)	Correction Factor (1)	Corrected Ratio (2) ±	Standard Error (S.E.)	Delt 6Li vs. IRM.016 ± S.E
F90-15C	3	68,298	4,951.3	0.899440	12.407 ± 0.022	± 0.022	-9.5 ± 1.8
F90-15C	3	66,410	4,862.9	0.908669	12.409 ± 0.029	± 0.029	-9.7 ± 2.4
F90-15C	4	65,861	4,794.8	0.905132	12.395 ± 0.044	± 0.044	-8.6 ± 3.5
F90-15C	4	65,373	4,738.0	0.899877	12.416 ± 0.049	± 0.049	-10.3 ± 3.9
FB.B1	3	143,215	11,598.2	0.995932	12.298 ± 0.014	± 0.014	-0.6 ± 1.2
FB.C1	3	99,754	7,750.1	0.970782	12.495 ± 0.005	± 0.005	-16.7 ± 0.4
RFB.C1	5	124,543	9,203.6	0.923136	12.492 ± 0.034	± 0.034	-16.4 ± 2.7
FB.C2	3	108,228	7,712.7	0.889977	12.489 ± 0.021	± 0.021	-16.2 ± 1.7
FB.C2	4	60,156	4,519.8	0.940181	12.513 ± 0.015	± 0.015	-18.2 ± 1.2
FB.C2-BLIND	3	105,552	7,434.4	0.882499	12.529 ± 0.008	± 0.008	-19.5 ± 0.6
FB.C2-BLIND	6	184,512	13,447.9	0.912323	12.518 ± 0.031	± 0.031	-18.5 ± 2.5
FB.D1	3	111,556	8,395.1	0.928442	12.337 ± 0.020	± 0.020	-3.9 ± 1.6
FB.D1	5	107,688	8,059.8	0.922943	12.332 ± 0.034	± 0.034	-3.4 ± 2.7
FB.D2	5	106,075	7,568.1	0.883401	12.382 ± 0.025	± 0.025	-7.5 ± 2.0
FB.D2	6	181,321	13,317.3	0.909952	12.389 ± 0.019	± 0.019	-8.1 ± 1.5
FB.D3	4	188,016	13,797.1	0.904747	12.329 ± 0.024	± 0.024	-3.2 ± 2.0
rep FB.D3	3	187,372	13,776.7	0.906340	12.327 ± 0.019	± 0.019	-3.0 ± 1.6
FB.D4	2	154,746	12,473.0	0.994509	12.338 ± 0.006	± 0.006	-3.9 ± 0.5
FB.D5	3	177,496	14,234.5	0.997750	12.441 ± 0.014	± 0.014	-12.3 ± 1.1
FB.D6	4	172,212	13,806.9	0.997353	12.440 ± 0.012	± 0.012	-12.2 ± 0.9
FB.D7	4	176,757	12,755.0	0.898137	12.446 ± 0.021	± 0.021	-12.7 ± 1.7
FB.D8	4	172,675	12,415.4	0.893238	12.423 ± 0.025	± 0.025	-10.8 ± 2.1
FB.D8	3	176,009	12,803.4	0.903165	12.416 ± 0.012	± 0.012	-10.2 ± 0.9
FB.G1	2	72,978	5,550.5	0.937871	12.331 ± 0.010	± 0.010	-3.3 ± 0.8
FB.G1	3	110,642	7,998.1	0.890697	12.322 ± 0.017	± 0.017	-2.6 ± 1.4
FB.G2	4	128,625	9,705.7	0.933982	12.378 ± 0.017	± 0.017	-7.1 ± 1.4
FB.G2	3	128,655	9,725.3	0.935385	12.374 ± 0.012	± 0.012	-6.8 ± 0.9
FB.M1	4	131,805	9,758.1	0.917623	12.395 ± 0.021	± 0.021	-8.5 ± 1.7
FB.M2	4	182,346	13,279.3	0.896321	12.308 ± 0.039	± 0.039	-1.5 ± 3.2
FB.R1	4	164,211	11,898.5	0.893240	12.328 ± 0.022	± 0.022	-3.1 ± 1.8

APPENDIX IV.1 CONT'D

Sample #	n	Net 7Li (cps)	Net 6Li (cps)	Correction Factor (1)	Corrected Ratio (2) ±	Standard Error (S.E.)	Delt 6Li vs. IRM-016 ± S.E.
FB.R2	3	179,253	12,942.0	0.894049	12.383 ±	0.076	-7.6 ± 6.1
HECTORITE	2	133,989	9,777.7	0.898632	12.314 ±	0.026	-2.0 ± 2.1
HECTORITE	6	258,522	14,025.8	0.667190	12.298 ±	0.037	-0.6 ± 3.0
HECTORITE	5	220,655	11,880.8	0.661245	12.281 ±	0.021	0.7 ± 1.7
HECTORITE	5	218,949	11,768.9	0.660906	12.295 ±	0.022	-0.4 ± 1.8
HECTORITE	3	254,607	6,935.1	0.334209	12.270 ±	0.027	1.7 ± 2.2

APPENDIX IV.2 - ICP-MS DATA FOR SAMPLES PREPARED BY ACID-LEACHING

Sample #	n	Net 7Li (cps)	Net 6Li (cps)	Correction Factor (f1)	Corrected Ratio (2)	Standard Error (S.E.)	Delt 6Li vs. IRM-016 ± S.E
1160(LEACHED)	6	175,627	13,733.3	0.956911	12.237 ± 0.023	5.1 ± 1.9	
1160(LEACHED)	5	201,704	15,815.2	0.968822	12.356 ± 0.018	6.1 ± 1.5	
1160(LEACHED)	4	84,824	6,377.3	0.914614	12.165 ± 0.057	10.2 ± 4.7	
HECT(LEACHED)	4	57,501	4,211.3	0.896447	12.240 ± 0.071	4.1 ± 5.8	
HECT(LEACHED)	3	39,783	3,118.6	0.962008	12.272 ± 0.020	1.5 ± 1.6	
HECT(LEACHED)	2	40,661	3,185.7	0.962053	12.279 ± 0.039	0.9 ± 3.2	
FB.C1(LEACHED)	5	54,589	4,789.0	0.970665	11.064 ± 0.016	99.7 ± 1.4	
FB.D1(LEACHED)	5	82,992	6,489.8	0.957737	12.248 ± 0.023	3.4 ± 1.9	
FB.D2 (LEACHED)	4	55,647	4,383.5	0.975364	12.382 ± 0.021	-7.5 ± 1.7	
FB.D2 (LEACHED)	3	60,916	4,816.5	0.977086	12.358 ± 0.039	-5.5 ± 3.2	
FB.G2(LEACHED)	5	71,011	5,628.2	0.926197	11.686 ± 0.049	49.2 ± 4.2	
FB.G2(LEACHED)	4	72,060	5,522.5	0.925316	12.074 ± 0.013	17.6 ± 1.1	
FB.G2 residue	6	44,217	3,483.0	0.971702	12.336 ± 0.067	-3.7 ± 5.4	
FB.G2 residue	3	41,888	3,297.2	0.970487	12.329 ± 0.067	-3.2 ± 5.4	
FB.G2 residue	5	48,418	3,812.6	0.973299	12.360 ± 0.043	-5.7 ± 3.5	
FB.G2 residue: column	6	118,969	9,946.3	1.027791	12.294 ± 0.013	-0.3 ± 1.0	

APPENDIX IV.3 - ICP-MS DATA FOR REFERENCE MATERIALS

Sample #	n	Net 7Li (cps)	Net 6Li (cps)	Correction Factor (1)	Corrected Ratio (2) ±	Standard Error (S.E.)	Delt 6Li vs. IRM-016 ± S.E
SVEC	4	688,235	56,384.3	1.007174	12.294 ± 0.043	0.043	-0.3 ± 3.5
SVEC	3	693,352	56,894.4	1.008752	12.293 ± 0.013	0.013	-0.3 ± 1.0
SVEC	3	705,053	57,946.3	1.010401	12.294 ± 0.014	0.014	-0.3 ± 1.1
SVEC	3	188,697	14,196.2	0.928092	12.336 ± 0.019	0.019	-3.8 ± 1.5
SVEC	5	190,782	14,318.2	0.925427	12.331 ± 0.035	0.035	-3.3 ± 2.8
SVEC	4	79,104	5,853.5	0.909456	12.290 ± 0.085	0.085	0.0 ± 6.9
SPEX	5	207,814	7,590.4	0.655528	17.948 ± 0.059	0.059	-460.4 ± 3.3
SPEX	5	208,238	7,612.9	0.656427	17.956 ± 0.063	0.063	-461.0 ± 3.5
LE-7	5	115,165	1,373.4	0.652663	54.729 ± 0.166	0.166	-3453.1 ± 3.0
LE-7	5	116,810	1,393.9	0.652931	54.717 ± 0.212	0.212	-3452.1 ± 3.9
LE-7	5	161,937	2,814.8	0.947600	54.532 ± 0.426	0.426	-3435.8 ± 7.8
LE-7	2	250,489	4,385.2	0.951711	54.364 ± 0.322	0.322	-3421.0 ± 5.9
LE-7	5	419,572	7,627.9	0.986754	54.277 ± 0.422	0.422	-3405.2 ± 7.8
LE-7	4	437,322	8,116.8	1.013096	54.584 ± 0.281	0.281	-3441.4 ± 5.2
LE-7	6	480,241	8,766.6	0.991268	54.303 ± 0.164	0.164	-3418.4 ± 3.0
LE-7	3	582,815	11,289.0	1.050539	54.236 ± 0.097	0.097	-3413.0 ± 1.8

(1) IRM-016 is the standard used to obtain the correction factor
 (2) the calculation of Standard Error is described in Appendix I

APPENDIX V - ELECTRON MICROPROBE DATA FOR SPODUMENE

Electron microprobe analyses were done on a Cambridge Microscan 5 electron probe operated at 20 kV accelerating potential and 30 nA absorbed current, measured on an amphibole standard. Analyses were performed using wavelength dispersive spectrometry, using K-alpha x-ray lines. Counting times were 100 seconds for minor elements, and 30 seconds for Si and Al. Si and Al were analyzed against a Kyanite standard, Fe, Mg and Na were analyzed against an amphibole standard (Kakanui USNM Hornblende), and Mn was analysed against a synthetic Mn_2SiO_4 standard. The Li values given in the following tables were obtained using ICP-MS.

APPENDIX V - ELECTRON MICROPROBE POINT ANALYSES OF SPODUMENES

	FBB1.1	FBB1.2	FBB1.3	FBB1.4	B1 AVG	FBC1.1	FBC1.2	FBC1.3	FBC1.4	C1 AVG	FBC2.1	FBC2.2
SiO2	64.05	64.11	64.43	64.52	64.28	64.37	64.39	64.56	64.09	64.35	64.71	64.11
Al2O3	27.04	27.64	27.63	27.70	27.53	26.66	26.74	27.03	26.74	26.81	25.85	26.30
Fe2O3	0.07	0.06	0.07	0.04	0.06	1.14	1.02	0.99	0.94	1.02	1.63	1.32
MnO	0.09	0.06	0.01	0.00	0.04	0.21	0.19	0.19	0.19	0.20	0.18	0.27
MgO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Na2O	0.05	0.09	0.12	0.08	0.09	0.16	0.15	0.16	0.16	0.16	0.12	0.13
Li2O	7.17	7.17	7.17	7.17	7.17	7.10	7.10	7.10	7.10	7.10	7.98	7.88
Total	98.49	98.15	98.75	98.53	98.23	99.88	99.61	100.10	99.26	99.66	100.49	100.13
Si	2.017	2.006	2.004	2.010	2.009	2.014	2.014	2.010	2.012	2.013	2.008	1.997
T site	2.017	2.006	2.004	2.010	2.009	2.014	2.014	2.010	2.012	2.013	2.008	1.997
Al	1.004	1.019	1.024	1.017	1.016	0.983	0.986	0.994	0.999	0.988	0.946	0.966
Fe 3+	0.002	0.001	0.002	0.001	0.002	0.027	0.024	0.023	0.022	0.024	0.036	0.031
M1 site	1.006	1.020	1.026	1.018	1.018	1.010	1.010	1.017	1.011	1.012	0.984	0.997
Mn	0.002	0.002	0.000	0.000	0.001	0.006	0.005	0.005	0.005	0.005	0.005	0.007
Mg	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Na	0.003	0.005	0.007	0.005	0.005	0.010	0.009	0.010	0.011	0.010	0.007	0.006
Li	0.008	0.002	0.007	0.008	0.001	0.003	0.003	0.000	0.006	0.003	0.006	1.000
M2 site	0.914	0.910	0.905	0.904	0.908	0.910	0.908	0.906	0.913	0.909	1.009	1.016

APPENDIX V CONT'D

	FEC2.3	FEC2.4	C2 AVG	FBD1.1	FBD1.2	FBD1.3	FBD1.4	D1 AVG	FBD2.1	FBD2.2	FBD2.3	FBD2.4
SiO2	84.58	84.28	84.41	85.35	88.19	85.91	85.83	85.77	83.83	83.17	83.59	83.58
Al2O3	28.49	28.45	28.27	27.32	27.34	27.47	27.40	27.38	27.78	27.23	27.81	27.80
Fe2O3	1.27	1.20	1.38	0.57	0.74	0.81	0.59	0.63	0.23	0.33	0.27	0.24
MnO	0.25	0.30	0.25	0.12	0.08	0.10	0.12	0.11	0.03	0.06	0.10	0.09
MgO	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.00	0.00	0.02
H2O	0.13	0.13	0.13	0.13	0.18	0.15	0.15	0.15	0.15	0.13	0.13	0.13
Li2O	7.98	7.98	7.98	7.44	7.44	7.44	7.44	7.44	7.21	7.21	7.21	7.21
Total	100.70	100.35	100.42	100.85	101.89	101.70	101.35	101.50	99.25	98.13	98.90	99.07
Si	1.990	1.997	1.998	2.012	2.018	2.015	2.013	2.015	1.997	2.000	1.997	1.994
T alts	1.990	1.997	1.998	2.012	2.018	2.015	2.013	2.015	1.997	2.000	1.997	1.994
Al	0.997	0.999	0.992	0.992	0.993	0.990	0.991	0.999	1.025	1.016	1.022	1.028
Fe 3+	0.030	0.028	0.032	0.013	0.017	0.014	0.014	0.015	0.005	0.008	0.006	0.008
M1 alts	0.997	0.997	0.994	1.005	1.000	1.004	1.006	1.004	1.030	1.024	1.028	1.034
Mn	0.007	0.008	0.007	0.003	0.002	0.003	0.003	0.003	0.001	0.002	0.003	0.002
Mg	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.001
Fe	0.008	0.008	0.008	0.008	0.011	0.009	0.009	0.009	0.009	0.008	0.008	0.008
Li	0.994	0.997	0.997	0.921	0.912	0.915	0.918	0.917	0.907	0.918	0.911	0.909
M2 alts	1.010	1.014	1.012	0.933	0.928	0.928	0.931	0.930	0.918	0.928	0.922	0.920

APPENDIX V CONT'D

	D2 AVG	FBD3.1	FBD3.2	FBD3.3	FBD3.4	D3 AVG	FBD4.1	FBD4.2	FBD4.3	FBD4.4	D4 AVG	FBD6.1
SiO ₂	63.54	64.35	63.73	64.48	63.75	64.08	64.09	63.73	63.98	63.77	63.89	64.60
Al ₂ O ₃	27.61	26.77	26.34	26.34	26.30	26.19	27.98	27.38	27.91	27.27	27.64	26.87
Fe ₂ O ₃	0.27	1.74	1.23	1.12	1.97	1.52	0.24	0.61	0.29	0.71	0.46	0.19
MnO	0.07	0.14	0.12	0.12	0.14	0.13	0.05	0.03	0.14	0.08	0.08	0.27
MgO	0.01	0.02	0.02	0.02	0.00	0.02	0.02	0.00	0.00	0.02	0.01	0.00
Na ₂ O	0.14	0.13	0.13	0.13	0.13	0.13	0.08	0.05	0.08	0.09	0.08	0.11
Li ₂ O	7.21	7.29	7.29	7.29	7.29	7.29	7.46	7.46	7.46	7.46	7.46	7.31
Total	98.84	99.44	98.86	99.50	99.59	99.35	99.92	99.26	99.86	99.40	99.61	99.36
Si	1.997	2.020	2.009	2.018	2.001	2.012	1.992	1.995	1.991	1.995	1.993	2.019
T site	1.997	2.020	2.009	2.018	2.001	2.012	1.992	1.995	1.991	1.995	1.993	2.019
Al	1.023	0.953	0.979	0.972	0.973	0.989	1.025	1.010	1.024	1.008	1.016	0.990
Fe 3+	0.006	0.041	0.029	0.026	0.047	0.036	0.006	0.014	0.007	0.017	0.011	0.004
M1 site	1.029	0.994	1.008	0.998	1.020	1.005	1.031	1.024	1.031	1.023	1.027	0.994
Mn	0.002	0.004	0.003	0.003	0.004	0.004	0.001	0.001	0.004	0.002	0.002	0.007
Mg	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.001	0.001	0.000
Fe	0.008	0.008	0.008	0.008	0.008	0.008	0.006	0.003	0.005	0.005	0.005	0.007
Li	0.911	0.920	0.924	0.918	0.920	0.921	0.932	0.939	0.934	0.939	0.938	0.919
M2 site	0.922	0.933	0.936	0.930	0.932	0.933	0.939	0.943	0.943	0.947	0.943	0.933

APPENDIX V CONT'D

	FB06.2	FB06.3	FB06.4	D6 AVG	FB06.1	FB06.2	FB06.3	FB06.4	D6 AVG	FB07.1	FB07.2	FB07.3
SiO2	64.73	64.22	64.67	64.56	64.11	64.20	64.05	63.94	64.08	64.00	64.43	64.33
Al2O3	27.42	26.66	26.89	26.96	26.08	27.44	27.57	27.47	27.64	27.80	27.91	27.72
Fe2O3	0.30	0.20	0.34	0.26	0.09	0.34	0.21	0.31	0.24	0.04	0.01	0.01
MnO	0.28	0.34	0.15	0.26	0.13	0.10	0.09	0.12	0.11	0.06	0.13	0.14
MgO	0.02	0.00	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
H2O	0.12	0.13	0.11	0.12	0.13	0.11	0.07	0.11	0.11	0.12	0.15	0.13
Li2O	7.31	7.31	7.31	7.31	7.36	7.36	7.36	7.36	7.36	7.66	7.66	7.66
Total	100.18	99.86	99.49	99.47	99.62	99.57	99.37	99.33	99.55	99.70	100.31	100.01
Si	2.009	2.018	2.019	2.016	1.993	2.003	2.001	2.000	1.999	1.992	1.994	1.996
T ails	2.009	2.016	2.019	2.016	1.993	2.003	2.001	2.000	1.999	1.992	1.994	1.996
Al	1.003	0.998	0.999	0.993	1.029	1.009	1.015	1.013	1.017	1.020	1.018	1.014
Fe 3+	0.007	0.005	0.008	0.006	0.002	0.008	0.005	0.007	0.006	0.001	0.000	0.000
M1 ails	1.010	0.993	0.997	0.999	1.031	1.017	1.020	1.020	1.022	1.021	1.018	1.014
Mn	0.007	0.009	0.004	0.007	0.003	0.003	0.002	0.003	0.003	0.002	0.003	0.004
Mg	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Ha	0.007	0.008	0.007	0.007	0.008	0.007	0.004	0.007	0.007	0.007	0.009	0.008
Li	0.912	0.924	0.918	0.918	0.920	0.924	0.925	0.926	0.924	0.959	0.953	0.956
M2 ails	0.927	0.941	0.930	0.933	0.932	0.935	0.932	0.937	0.934	0.969	0.966	0.969

APPENDIX V CONT'D

	FB07.4	D7 AVG	FB08.1	FB08.2	FB08.3	FB08.4	D8 AVG	FB01.1	FB01.2	FB01.3	FB01.4	G1 AVG
SiO2	64.24	64.25	65.93	65.78	65.65	64.75	65.53	65.72	65.67	65.01	64.84	65.31
Al2O3	27.76	27.80	27.89	27.80	27.61	27.34	27.66	27.15	27.12	27.03	26.98	27.08
Fe2O3	0.01	0.02	0.38	0.37	0.24	0.39	0.34	0.71	0.64	0.89	0.73	0.69
MnO	0.13	0.12	0.25	0.21	0.15	0.08	0.17	0.08	0.12	0.13	0.06	0.10
MgO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.01
Na2O	0.13	0.13	0.12	0.13	0.09	0.08	0.11	0.12	0.18	0.18	0.12	0.15
Li2O	7.68	7.68	7.61	7.61	7.61	7.61	7.61	7.21	7.21	7.21	7.21	7.21
Total	99.95	99.99	102.18	101.92	101.37	100.27	101.44	101.01	100.94	100.30	99.94	100.55
Si	1.995	1.994	2.008	2.006	2.010	2.005	2.007	2.023	2.023	2.016	2.017	2.020
T site	1.995	1.994	2.008	2.006	2.010	2.005	2.007	2.023	2.023	2.016	2.017	2.020
Al	1.016	1.017	1.000	0.999	0.997	0.998	0.999	0.995	0.995	0.990	0.999	0.997
Fe 3+	0.000	0.000	0.008	0.008	0.006	0.009	0.008	0.016	0.015	0.016	0.017	0.016
M1 site	1.016	1.017	1.008	1.007	1.003	1.007	1.006	1.001	1.000	1.006	1.006	1.003
Mn	0.003	0.003	0.008	0.005	0.004	0.002	0.004	0.002	0.003	0.003	0.002	0.003
Mg	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000
Na	0.008	0.008	0.007	0.008	0.005	0.005	0.006	0.007	0.011	0.011	0.007	0.009
Li	0.997	0.998	0.991	0.993	0.997	0.948	0.937	0.992	0.993	0.999	0.992	0.997
M2 site	0.998	0.998	0.945	0.947	0.947	0.958	0.949	0.992	0.997	0.913	0.911	0.908

APPENDIX V CONT'D

	FBG2.1	FBG2.2	FBG2.3	FBG2.4	G2 AVG	FBM1.1	FBM1.2	FBM1.3	FBM1.4	FBM1.5	M1 AVG	FBR1.1
SiO2	84.24	84.33	84.85	84.41	84.41	84.84	84.05	85.20	84.99	85.01	84.82	85.07
Al2O3	27.17	27.59	27.85	27.80	27.83	28.13	28.51	28.68	28.72	28.83	28.57	27.25
Fe2O3	0.01	0.01	0.03	0.01	0.02	1.39	0.81	0.89	0.80	0.84	0.85	0.31
MnO	0.00	0.00	0.01	0.00	0.00	0.22	0.01	0.03	0.00	0.01	0.05	0.15
MgO	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Na2O	0.12	0.05	0.09	0.05	0.08	0.13	0.09	0.09	0.16	0.05	0.10	0.12
Li2O	7.25	7.25	7.25	7.25	7.25	7.45	7.45	7.45	7.45	7.45	7.45	8.83
Total	98.79	99.25	99.98	99.52	99.39	100.16	98.92	100.34	100.12	100.19	99.95	99.55
Si	2.018	2.009	2.005	2.006	2.009	2.018	2.012	2.020	2.018	2.018	2.017	2.031
T alts	2.018	2.009	2.005	2.006	2.009	2.018	2.012	2.020	2.018	2.018	2.017	2.031
Al	1.005	1.016	1.022	1.021	1.016	0.959	0.982	0.974	0.978	0.981	0.975	1.002
Fe 3+	0.000	0.000	0.001	0.000	0.000	0.033	0.019	0.021	0.019	0.020	0.022	0.007
M1 alts	1.005	1.016	1.023	1.021	1.016	0.982	1.001	0.985	0.997	1.001	0.997	1.009
Mn	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.001	0.000	0.000	0.001	0.004
Mg	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Ha	0.007	0.003	0.005	0.003	0.005	0.008	0.005	0.005	0.010	0.003	0.008	0.007
Li	0.915	0.911	0.905	0.908	0.910	0.933	0.941	0.928	0.930	0.929	0.932	0.932
M2 alts	0.922	0.915	0.910	0.911	0.915	0.947	0.946	0.934	0.940	0.932	0.940	0.844

APPENDIX V CONT'D

	FBR1.2	FBR1.3	FBR1.4	R1 AVG	FBR2.1	FBR2.2	FBR2.3	RBR2.4	R2 AVG
SiO ₂	65.16	65.33	65.37	65.23	64.71	64.97	65.01	65.16	64.96
Al ₂ O ₃	27.13	27.29	27.46	27.28	26.98	27.44	27.04	27.08	27.14
Fe ₂ O ₃	0.56	0.40	0.64	0.48	0.24	0.34	0.39	0.28	0.32
MnO	0.21	0.26	0.23	0.21	0.08	0.13	0.08	0.08	0.08
MgO	0.02	0.02	0.02	0.02	0.02	0.02	0.12	0.00	0.04
Na ₂ O	0.16	0.15	0.13	0.14	0.09	0.12	0.13	0.09	0.11
Li ₂ O	6.63	6.63	6.63	6.63	7.55	7.55	7.55	7.55	7.55
Total	99.87	100.08	100.48	100.00	99.65	100.57	100.30	100.23	100.19
Si	2.030	2.030	2.025	2.029	2.014	2.008	2.013	2.017	2.013
T site	2.030	2.030	2.025	2.029	2.014	2.008	2.013	2.017	2.013
Al	0.998	1.000	1.003	1.000	0.990	0.999	0.997	0.998	0.991
Fe 3+	0.013	0.008	0.015	0.011	0.008	0.008	0.009	0.007	0.008
M1 site	1.009	1.009	1.018	1.011	0.998	1.007	0.998	0.995	0.999
Mn	0.006	0.007	0.006	0.006	0.002	0.003	0.002	0.002	0.002
Mg	0.001	0.001	0.001	0.001	0.001	0.001	0.006	0.000	0.002
Fe	0.010	0.009	0.008	0.009	0.005	0.007	0.008	0.005	0.006
Li	0.831	0.829	0.826	0.830	0.945	0.938	0.940	0.940	0.941
M2 site	0.848	0.846	0.841	0.845	0.953	0.949	0.956	0.947	0.951