

Limited lithium isotopic fractionation during progressive metamorphic dehydration in metapelites: A case study from the Onawa contact aureole, Maine

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Abstract

The major, trace element, and Li isotopic compositions of granodiorite and metapelites from the Onawa pluton and surrounding contact aureole have been measured to document the behavior of Li and its isotopes during progressive metamorphic dehydration. Major and trace element concentrations in metapelites of the contact aureole change little, while loss on ignition (LOI) decreases with increasing metamorphic grade, which ranges from regional chlorite-zone metamorphism far removed from the pluton to partially melted rocks adjacent to the pluton. Lithium concentrations in metapelites from all zones correlate with LOI and abundances of the main Li-bearing minerals, chlorite + biotite + muscovite, decreasing by a factor of two (from 130 ppm far removed from the pluton to 64 ppm adjacent to the pluton). In contrast, Li isotopic compositions remain relatively unchanged across the aureole ($\delta^7\text{Li} = -3.5$ to $+1.0$), and are comparable to the range observed in schists and unmetamorphosed shales. Compared to the surrounding metasediments, the granodiorite has a lower Li content (45 ppm) and a comparable $\delta^7\text{Li}$ value of -0.2 , similar to those of other granites and the average upper crust (0 ± 2).

These observations are consistent with the removal of Li from metapelites via Rayleigh distillation during progressive metamorphic dehydration, with isotopic fractionation factors between fluids and rocks ranging between 1.001 and 1.004. These values are similar to those of a recent experimental study and produce isotopic fractionation that is barely beyond analytical uncertainty ($\pm 1\%$) for the observed degree of Li depletion. The good correlations between Li concentrations and LOI with mineralogical abundances reflect the importance of mineralogy in controlling Li concentrations and isotopic compositions of metamorphic rocks. Comparison of these results with those from a study of a contact halo around the Tin Mountain pegmatite suggests that the nature of the intrusion plays a critical role in controlling the behavior of Li in country rocks. Large, diffusive-driven isotopic fractionation over a small scale is expected to occur when rocks are infiltrated by Li-rich magmatic fluids, while metamorphic devolatilization results in minor isotopic fractionation on the aureole scale. Published by Elsevier B.V.

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1. Introduction

In order to fully utilize Li isotopes as geochemical tracers, it is necessary to characterize the Li isotopic compositions of different geological reservoirs, and quantify the magnitude of isotopic fractionations for various conditions. The continental crust appears to have a lighter Li isotopic composition than the upper mantle, from which it was derived (Teng et al., 2004a,b). Given that Li isotopes do not fractionate during high- T igneous differentiation (Tomascak et al., 1999), juvenile crust and the mantle should have identical Li isotopic compositions. The isotopically light continental crust, therefore, is likely a result of post-formational processes, such as weathering, low- T intracrustal melting and metamorphism. Recent studies have demonstrated large Li isotopic fractionation during diffusion (Richter et al., 2003; Lundstrom et al., 2005; Teng et al., 2006a), terrestrial weathering (Pistiner and Henderson, 2003; Huh et al., 2004; Rudnick et al., 2004; Kisakurek et al., 2004), hydrothermal alteration (Chan et al., 1992, 1993, 1994; Seyfried et al., 1998; Chan and Kastner, 2000; Chan et al., 2002; James et al., 2003; Bouman et al.,

2004; Foustoukos et al., 2004; Williams and Hervig, 2005) and smaller Li isotopic fractionation during granite differentiation (Bryant et al., 2004; Teng et al., 2004a, 2006b). The nature of Li isotopic fractionation during progressive metamorphism, however, is not yet well established.

Studying Li isotopic fractionation during metamorphism will shed light on the Li isotopic composition and evolution of the crust and Li behavior during subduction processes. Some eclogites and granulites have very light Li isotopic compositions (down to -18%) (Zack et al., 2003; Teng et al., 2004b), while forearc serpentinites, which are interpreted to have interacted with slab-derived fluids, have both light and heavy Li isotopic compositions (Benton et al., 2004). These observations have been explained by Li isotopic fractionation associated with metamorphic dehydration, with isotopically heavy Li preferring fluids to rocks. However, to date, no comprehensive study of Li isotopic fractionation as a function of metamorphic grade has been carried out.

We present here the Li concentration and isotopic data for a suite of metapelites from the well-

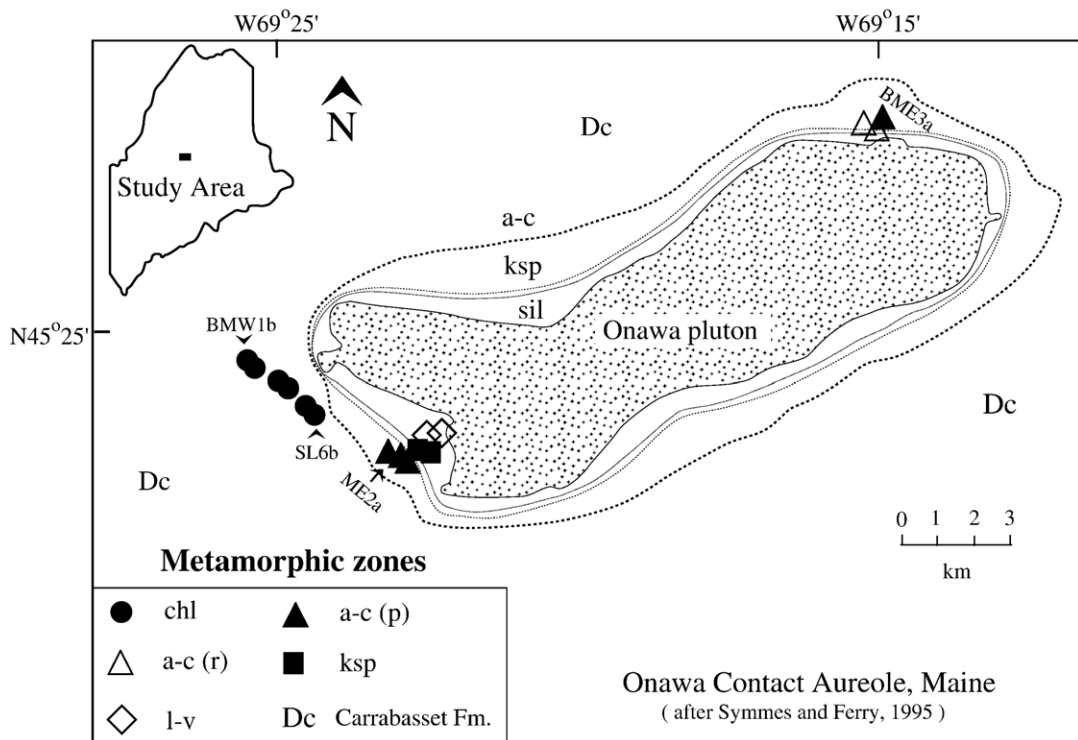


Fig. 1. Metamorphic map of study area with sample locations. Inset at upper left shows location of field area in central Maine. Sample locations and isograds are illustrated. Modified from Symmes and Ferry (1995). See Table 1 for abbreviations of metamorphic zones.

characterized contact aureole around the Onawa pluton, Maine, USA. The Onawa aureole has a relatively simple geological setting and metamorphic history that makes it an ideal field laboratory for studying the isotopic consequences of metamorphism. Contact metamorphism in the Onawa aureole occurred as a suite of dehydration reactions occurring at $P \sim 0.3$ GPa and T from ~ 500 to ~ 650 °C, and produced significant partial melting in the highest grade rocks (Symmes and Ferry, 1995). Our results demonstrate that although a large amount of Li was released into fluids during metamorphic dehydration, $\delta^7\text{Li}$ changes little, suggesting that Li isotopic fractionation at this temperature range is small and reflecting the importance of mineralogy in controlling Li concentrations and isotopic compositions of metamorphic rocks.

2. Geological background and samples

At the surface, the Onawa pluton is an $\sim 5 \times 15$ km composite intrusion comprised of quartz diorite and granodiorite. Intrusion of this pluton into chlorite-zone regional metasedimentary rocks of the Carrabassett Formation during the late stages of the Acadian orogeny produced an ~ 1.5 km wide contact aureole (Philbrick, 1936; Symmes and Ferry, 1995). The Carrabassett Formation consists of pelites and graywackes interbedded at a scale of 1 to 100 cm. Symmes and Ferry (1995) delineated five metamorphic zones in the aureole based on mineral assemblages (Fig. 1): chlorite zone (chl, >1500 m from the pluton, subject to regional metamorphism only), andalusite–cordierite zone (a–c, 800–1500 m, start of the contact metamorphism), potassium feldspar zone (ksp, 500–800 m), sillimanite zone (sil, 300–500 m) and leucocratic-vein zone (l–v, <300 m, end of contact metamorphism). The a–c zone can be further divided into two subzones: the prograde zone (a–c (p)) with fresh cordierite and/or no chlorite; and the retrograde zone (a–c (r)), in which cordierite is replaced by chlorite (Symmes and Ferry, 1995). Mineralogy and texture of each zone have been thoroughly studied by Symmes and Ferry (1995) and a brief description is given below.

All metapelites contain muscovite, quartz, plagioclase and ilmenite, with minor quantities of tourmaline and zircon (Symmes and Ferry, 1995; Table 1). Chlorite and graphite are mainly concentrated in the outer zones (chl and a–c), while biotite, cordierite and andalusite generally appear in all zones except the chl zone; potassium feldspar and sillimanite occur in the inner zones (ksp, sil and l–v; Symmes and Ferry, 1995; Table 1). The leucocratic veins, which range from 13 to 40 vol.%

in the l–v zone, are dominated by quartz, potassium feldspar, plagioclase and cordierite (Symmes and Ferry, 1995). Based on field observations, mineral textures, major-element geochemistry, reaction stoichiometry and geothermometry, Symmes and Ferry (1995) suggest that these veins represent crystallized, locally derived partial melts. The stoichiometry and progress of mineral reactions were used to calculate the time-integrated fluid flux for the l–v zone samples, which ranged from 0.9 to 3.1×10^4 mol/cm²; the fluid was mainly composed of H₂O, and flowed up-temperature from the outer aureole (Symmes and Ferry, 1995; Table 12). Peak metamorphic conditions, estimated from mineral equilibria, are $P \sim 0.3$ GPa, with T ranging from 480–540 °C in the andalusite–cordierite zone to 640–650 °C in the leucocratic-vein zone, with uncertainties of ~ 10 –20 °C (Symmes and Ferry, 1995; Tables 8 and 9).

Due to the small scale of the aureole (~ 1.5 km), metapelitic rocks can be sampled from the same lithologic units at different grades. Whole rock samples from the igneous intrusion and all zones except the

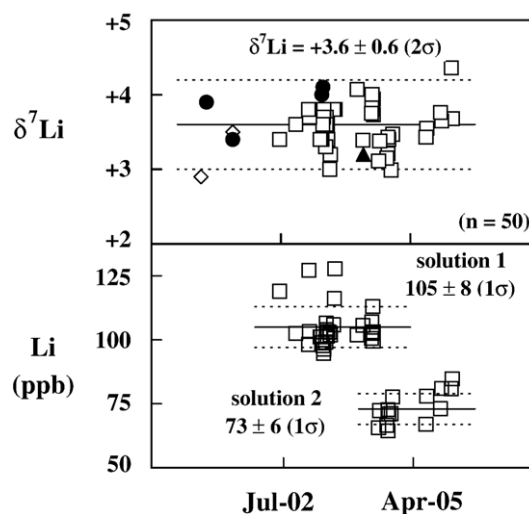


Fig. 2. Compilation of analyses of four preparations of shale standard AO-12, from the Amadeus Basin, Australia (Teng et al., 2004a), illustrating long-term analytical precision of the methods used in this study. Different symbols denote analyses from separate digestions, with Li concentrations of solutions ranging from 50 to 150 ppb. Filled-symbols are samples taken through the column chemistry procedure described in Teng et al. (2004a) and all other samples were taken through the column chemistry procedure described in Rudnick et al. (2004). The overall mean $\delta^7\text{Li} = 3.6 \pm 0.6$ (2σ). The uncertainty for Li concentration measurement is $< \pm 10\%$ (1σ) based on measurements of two separate AO-12 solutions of different concentrations. Solid lines represent the average $\delta^7\text{Li}$ and Li while dashed lines indicate 2σ precision limits for $\delta^7\text{Li}$ and 1σ precision limits for Li concentration.

Table 1
Major, trace element and Li isotopic compositions of samples from the Onawa contact aureole, Maine

Sample ¹	Zone ²	Li ³	$\delta^7\text{Li}^4$	SiO ₂	TiO ₂	Al ₂ O ₃	FeO ⁵	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI ⁶	Total	CIA ⁷
BMW1b	Chl	106	-1.0	67.4	1.0	15.4	6.3	0.1	2.1	0.3	1.3	2.9	0.1	3.0	99.9	73
SL15a	Chl	97	-2.2	64.5	1.0	17.4	5.8	0.1	2.1	0.4	1.2	3.9	0.1	3.4	99.9	72
SL14b	Chl	87	-1.9	71.9	0.9	15.0	5.5	0.1	1.3	0.1	0.9	2.5	0.1	2.6	100.9	78
BMW2b	Chl	131	-1.4	59.5	1.0	19.7	7.5	0.1	2.3	0.6	1.4	3.6	0.2	3.9	99.8	74
BMW3a	Chl	93	-1.4	65.4	1.0	17.3	6.4	0.1	1.7	0.3	1.1	3.3	0.1	3.2	99.9	75
SL6b	Chl	108	-2.0	58.3	1.2	21.0	7.5	0.1	2.1	0.4	1.0	4.3	0.2	4.0	100.1	76
BME1a	a-c (r)	124	+0.9	62.0	1.1	19.6	7.0	0.1	1.8	0.3	1.1	3.7	0.2	3.2	100.1	77
BME5a	a-c (r)	117	-1.6	64.6	1.1	18.6	6.8	0.1	1.6	0.2	0.9	3.5	0.1	2.6	100.1	78
ME2a	a-c (p)	91	-1.8	66.4	1.1	17.8	6.7	0.1	1.8	0.4	1.3	3.2	0.2	1.1	100.1	75
ME2b	a-c (p)	82	-2.4	67.0	1.0	17.5	6.1	0.1	1.8	0.5	1.4	3.3	0.1	1.2	100.0	73
ME2d	a-c (p)	82	-2.6	63.0	1.1	19.4	6.9	0.1	2.1	0.9	2.0	2.5	0.2	1.8	100.0	73
BME3a	a-c (p)	73	-1.8	66.3	0.9	14.9	7.0	0.2	2.9	1.9	2.1	2.6	0.2	1.1	100.1	62
ONA-2	ksp	65	-2.1	60.2	1.2	20.6	7.6	0.1	2.5	0.6	1.6	4.1	0.1	1.4	100.0	72
ONA-5	ksp	64	-3.5	63.7	1.1	19.3	6.7	0.1	2.0	0.3	1.3	4.2	0.1	1.1	99.9	73
BMW5a	l-v	94	-0.5	61.7	1.1	20.5	6.7	0.1	1.7	0.3	1.7	4.3	0.2	1.8	100.1	73
BMW6a	l-v	82	-1.7	62.3	1.1	20.3	7.5	0.1	2.1	0.4	1.2	3.7	0.2	1.1	100.0	77
ONA-11	pluton	45	-0.2	58.8	1.4	18.0	7.2	0.1	2.4	5.6	3.0	3.0	0.2	0.3	100.0	50

Sample	Zone	Ni	Cr	Sc	V	Ba	Rb	Sr	Zr	Y	Nb	Ga	Cu	Zn	Pb	La	Ce	Th	Nd
BMW1b	Chl	58	112	15	121	445	134	114	435	42	16.7	19	14	97	15	44	90	13	40
SL15a	Chl	66	122	21	164	519	190	160	213	35	17.7	25	13	116	23	57	111	15	49
SL14b	Chl	55	97	17	142	474	152	137	257	37	18.0	22	13	98	19	55	101	13	47
BMW2b	Chl	58	112	20	162	683	173	166	260	42	19.6	26	1	105	31	54	110	16	48
BMW3a	Chl	60	119	19	172	560	165	157	252	39	19.3	27	8	114	25	54	110	15	47
SL6b	Chl	65	121	21	173	623	201	133	287	47	20.9	28	13	112	32	60	119	16	52
BME1a	a-c (r)	81	123	17	126	403	126	153	226	37	13.8	20	5	97	21	42	77	11	37
BME5a	a-c (r)	48	102	18	142	522	168	144	275	39	18.3	24	25	78	26	49	96	15	43
ME2a	a-c (p)	42	82	14	109	378	119	99	331	34	15.8	18	24	76	17	40	81	12	36
ME2b	a-c (p)	64	115	17	140	597	173	114	304	40	18.5	23	34	117	18	52	96	14	43
ME2d	a-c (p)	51	102	18	139	483	140	132	267	39	19.1	23	28	101	25	48	91	13	41
BME3a	a-c (p)	58	103	17	136	484	135	136	301	38	18.4	22	22	98	24	46	91	13	41
ONA-2	ksp	24	60	22	127	388	123	199	403	44	12.7	24	17	87	18	40	82	11	39
ONA-5	ksp	69	133	21	179	589	191	153	256	43	20.9	25	2	119	27	64	119	16	56
BMW5a	l-v	59	136	19	154	423	133	206	282	35	20.4	25	3	110	24	51	103	15	46
BMW6a	l-v	56	110	19	161	553	180	148	224	38	18.3	26	7	94	25	54	100	14	43
ONA-11	pluton	58	112	19	154	603	180	138	253	40	19.3	27	14	103	24	49	99	14	44

Analytical uncertainty is <1% for the major elements and <10% for the minor and trace elements (Johnson et al., 1999). Oxides are reported in wt.%, minor and trace elements in ppm (ug/g).

1. Samples are listed in order of decreasing distance from the pluton.

2. chl = chlorite; a-c (p) = andalusite–cordierite (prograde); a-c (r) = andalusite–cordierite (retrograde); ksp = potassium feldspar; l-v = leucocratic vein; pluton = Onawa intrusion.

3. Li measured by comparison of signal intensities with 50 or 100 ppb L-SVEC with uncertainty <±10% (1σ).

4. Analytical uncertainty is <±1‰ (2σ), based on both pure Li solutions and natural rocks (see text for details).

5. FeO: total Fe as FeO.

6. LOI: loss on ignition at 900 °C.

7. CIA is the molar Al₂O₃/(Al₂O₃+K₂O+Na₂O+CaO*)×100, where CaO* refers to Ca in silicate only and not contained in carbonate and phosphate (Nesbitt and Young, 1982). McLennan's (1993) correction to the measured CaO content for the presence of Ca in carbonates and phosphates is used here. CIA value increases with the degree of weathering. Unweathered igneous rocks have CIA ~50 while shales have higher values between 60 and 80 (Nesbitt and Young, 1982).

sillimanite zone have been measured. These samples are the same as those used in Wing et al. (2003) and Marchildon and Brown (2001), and taken from the same outcrops as those described in Symmes and Ferry (1995).

3. Analytical methods

Major and minor element concentrations were determined by X-ray fluorescence (XRF) analysis using a Li-tetraborate fused bead technique at the Geoanalytical

Laboratory of Washington State University. Analytical uncertainty is <1% for the major elements and <10% for the minor and trace elements (Johnson et al., 1999). Lithium analyses were performed at the Geochemistry Laboratory of the University of Maryland, College Park. Procedures for sample dissolution, column chemistry, and instrumental analysis are the same as those reported in Teng et al. (2006b).

The external precision of Li isotopic analyses, based on 2σ of repeat runs of pure Li standard solutions and rock solutions, is $\leq \pm 1.0\%$. For example, pure Li standard solutions (IRMM-016 and UMD-1), which are measured during each analytical session ($n=5$ for each session), have values falling within previous established ranges ($-0.1 \pm 0.2\%$ and $+54.7 \pm 1\%$, respectively Teng et al., 2004a); rock sample AO-12, a shale from the Amadeus Basin, Australia (part of the PAAS group of Nance and Taylor (1976)) gives $\delta^7\text{Li} = +3.6 \pm 0.6$ (2σ , $n=50$ runs with 4 replicate sample preparations over a three-year period) (Fig. 2). While the long-term reproducibility of AO-12 suggests that a significant reduction in the overall uncertainty of a $\delta^7\text{Li}$ analysis may be possible, external reproducibility tests on a range of in-house and international standards indicate that our best current uncertainty is somewhat larger, at $\sim \pm 1.0\%$. This value is used here. The uncertainty of Li concentration measurements, determined by voltage comparison between sample solution and that measured for 50 or 100 ppb L-SVEC standard solution and then adjusting for sample weight, is $\leq \pm 10\%$ (1σ) (Fig. 2).

4. Results

Lithium concentrations and isotopic compositions of all samples are reported in Table 1, along with the major and trace element concentrations, metamorphic grade and chemical index of alteration (CIA) (see footnote of Table 1 for explanation of CIA).

Major and trace element concentrations in the metapelites vary little and are similar to values previously reported (Symmes and Ferry, 1995; Table 3) (Fig. 3). Loss on ignition (LOI) values decrease with increasing metamorphic grade, with samples from the retrograde andalusite–cordierite zone (a–c (r)) having significantly higher values than those from the prograde zone (a–c (p)) (Table 1). The homogeneous chemical compositions result in a small range in CIA values, from 72 to 78, with an average of 75 ± 2 , except sample BME3a, which has a value of 62. The reason for this significantly lower value is unknown. Lithium concentrations correlate positively with LOI and decrease with progressive metamorphism towards the pluton, while samples from the a–c (r) zone have higher Li concentrations than their prograde counterparts and samples from the l–v zone have higher Li concentration than those from the ksp zone (Fig. 4). Lithium isotopic compositions remain relatively constant, from -3.5 to -1.0 for samples in prograde metamorphic zones and -1.7 to $+0.9$ for samples from a–c (r) and l–v zones (Fig. 4). Overall, the Li concentrations and isotopic compositions of the Onawa metapelites fall within the

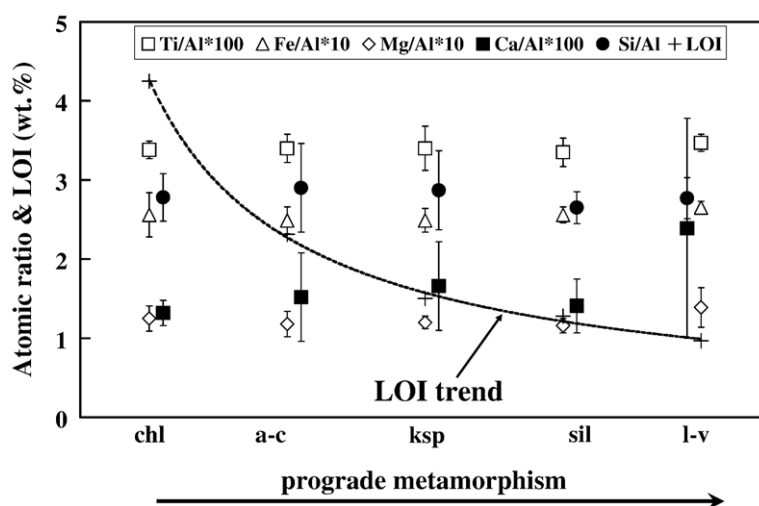


Fig. 3. Plots of mean whole-rock loss on ignition (LOI) and atomic i/Al for all metapelite samples in all zones, where i=Ti, Fe, Mg, Ca and Si; data for means and standard deviations are from Symmes and Ferry (1995), which are based on more samples than this study; samples measured in this study (Table 1) show a similar trend. LOI is an indication of total water content, which changes systematically with metamorphic grade. See Table 1 for abbreviations of metamorphic zones.

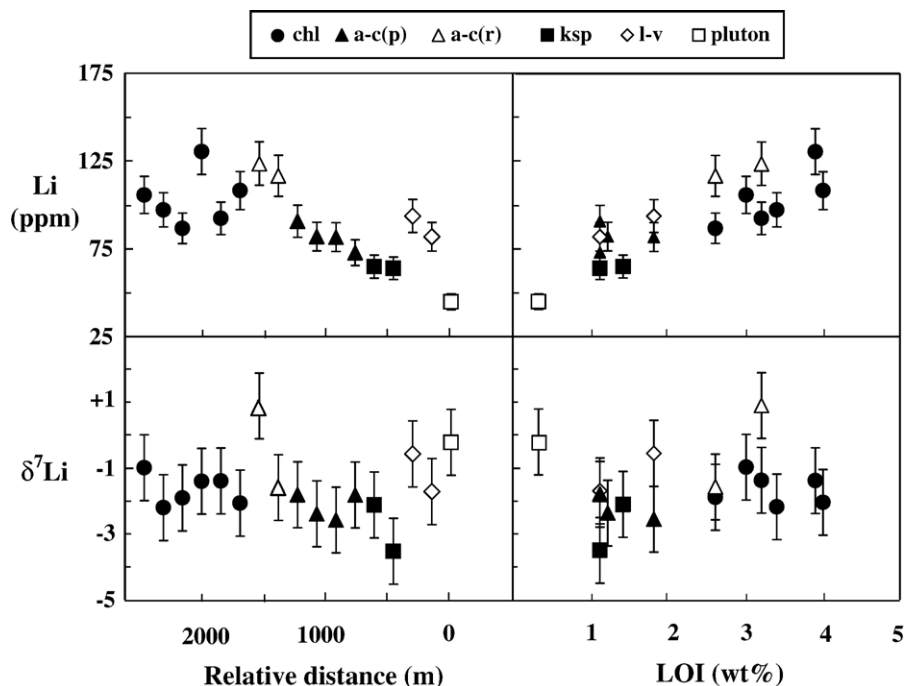


Fig. 4. Plots of Li, $\delta^7\text{Li}$ versus LOI versus LOI, and distance; filled symbols represent metapelites that experienced prograde metamorphism while open symbols represent pluton (granodiorite) and samples reacted with retrograde fluids; data from Table 1. See Table 1 for abbreviations of metamorphic zones.

range observed in typical post-Archean shales and schists (Teng et al., 2004a; 2006b). The granodiorite sample, taken from the Onawa pluton, has 45 ppm Li and $\delta^7\text{Li} = -0.2$, falling in the range typical of granites (Bryant et al., 2004; Teng et al., 2004a; 2006b).

5. Discussion

The Li concentrations and $\delta^7\text{Li}$ values of the Onawa metapelites, which overlap those of schists and unmetamorphosed shales (Teng et al., 2004a, 2006b), may reflect their sedimentary protolith. They may also reflect the influence of processes that have acted upon the Onawa metapelites at various times, such as variable degrees of weathering of the protolith, dehydration during the regional and contact metamorphism, infiltration of these metapelites by magmatic fluids exsolved from the intrusion and/or metamorphic fluids during contact metamorphism. In this section, we first explore how these different processes may affect Li concentration and isotopic composition of the metapelites, and then discuss the general behavior of Li during metamorphism. Finally, we compare this study with the results of a study of Li in country rocks adjacent to a Li-rich pegmatite to illustrate how the character of the

igneous intrusion exerts a strong control on the behavior of Li in contact metamorphic rocks.

5.1. Lithium in metapelites from the Onawa contact aureole

The metapelites of the Onawa aureole are all from the same lithologic unit and have constant major-element compositions across the different metamorphic grades, which rules out significant protolith heterogeneity. This is further supported by the constant CIA values (75 ± 2) for samples studied here, which indicates their protoliths represent similar degrees of weathering. Accordingly, although Li concentrations and isotopic compositions of terrestrial rocks vary significantly (Tomascak, 2004), rocks of the chl zone in the aureole should not have significantly different Li concentrations and isotopic compositions. Statistical tests confirm this, and indicate that the chl-zone metapelites sample a uniform population characterized by a mean Li concentration of 100 ± 19 ppm (2σ , $\chi^2_5 = 1.87^{2.56}_{0.17}$, where the right-hand subscript and superscript refer the range between which 95% of the expected reduced χ^2 values would be found for a sample set with 5 degrees of freedom) and a mean $\delta^7\text{Li}$ value of -1.7 ± 0.9 (2σ , $\chi^2_5 = 0.82^{2.56}_{0.17}$). This

statistical uniformity does not carry over to higher-grade rocks and requires an examination of the various metamorphic processes that may have influenced the Li concentration and isotopic composition of rocks in the aureole.

5.1.1. Metamorphic fluid infiltration

Flow of metamorphic fluids along a temperature gradient, with local isotopic equilibrium between fluids and rocks during metamorphism, has been proposed to explain large oxygen isotopic variations observed in metamorphic terranes and contact aureoles, where the difference in $\delta^{18}\text{O}$ between metamorphic rocks and their low-grade equivalents is larger than what can be explained by mineral reactions and the effects of Rayleigh distillation (Dipple and Ferry, 1992). For example, under local fluid–rock isotopic equilibrium, a time-integrated fluid flux of 1×10^5 mol/cm² flowing along a linear T gradient from 300–600 °C will cause $\delta^{18}\text{O}$ in a quartzo-feldspathic rock to decrease by $\sim 5\%$ (Dipple and Ferry, 1992); devolatilization alone, however, only produces an $\sim 1\%$ variation (Rumble, 1982). The degree of isotopic change produced by metamorphic fluid infiltration depends on the time-integrated fluid flux, the temperature gradient along the flow path, the temperature dependence of the isotopic fractionation factor, α (here, $\alpha^{\text{fluid/rock}} = [{}^7\text{Li}/{}^6\text{Li}]_{\text{fluid}} / [{}^7\text{Li}/{}^6\text{Li}]_{\text{rock}}$), the isotopic composition of the fluid entering the metamorphic flow system, and the partitioning behavior of the element of interest (Dipple and Ferry, 1992). As a rule of thumb, the magnitude of final isotopic shift is directly proportional to all these factors (i.e., higher fluid flux, larger temperature gradient, greater T dependence of α , a disequilibrium input fluid and an element that is strongly partitioned into the fluid will all lead to more significant isotopic shifts). From these insights we can consider the potential shift in Li isotopic composition for the Onawa aureole as a function of fluid flux, α and changes in temperature.

The up-temperature, time-integrated fluid fluxes that induced melting in the leucocratic-vein zone of the Onawa contact aureole are estimated to range from 0.9 to 3.1×10^4 mol/cm² (Symmes and Ferry, 1995). These flux magnitudes will not lead to much O isotopic change at contact metamorphic temperatures (Dipple and Ferry, 1992). However, Li is preferentially taken up by aqueous fluids (Brenan et al., 1998) and the amount of Li in metamorphic rocks is much less than the amount of O; both factors could make Li more isotopically sensitive to metamorphic fluid flow. On the other hand, the experiments of Wunder et al. (2006) indicate a minor T dependence to fluid–mineral Li isotopic fractionation

factors at contact metamorphic conditions (e.g., when temperature increases from 480 to 650 °C, Li isotopic fractionation between hydrothermal fluids and spodumene will change from -3.6% to -2.5%). Because of this small difference in fractionation, flow of a metamorphic fluid under local isotopic equilibrium might not change the $\delta^7\text{Li}$ values beyond analytical uncertainty in the aureole. For example, Dipple and Ferry (1992) found that infiltration of rocks by metamorphic fluids results in little modification of carbon and sulfur isotopic compositions because of the small isotopic fractionation factors for C and S between carbonates and CO_2 and iron sulfides and H_2S at metamorphic temperatures. Sensitivity tests using the formalism of Dipple and Ferry (1992), the estimated time-integrated fluid fluxes of Symmes and Ferry (1995), and the fractionation factor calibration of Wunder et al. (2006) indicate that up-temperature equilibrium fluid flow would produce slight ${}^7\text{Li}$ enrichment (up to $\sim 1\%$) in the rocks in the Onawa aureole with increasing metamorphic grade (cf. Figs. 4 and 5 of Dipple and Ferry, 1992). This enrichment is due to the sign of the T -derivative of the fractionation factor of Wunder et al. (2006) and is opposite to the trend suggested by our observations (Fig. 4). However, this enrichment is very slight, indicating that the small magnitude of the fractionation factor for Li isotopes trumps the enhanced isotopic sensitivity implied by Li partitioning behavior. Thus, like sulfur and carbon isotopes, it appears that Li isotopes will not be greatly affected by flow of metamorphic fluids under local fluid–rock equilibrium. Other processes, such as metamorphic dehydration or the infiltration of isotopically exotic fluids, are likely to be more important agents of Li isotopic fractionation in contact metamorphic environments.

5.1.2. Decreasing Li concentration in metapelites with prograde metamorphism

Most prograde metamorphic reactions in metapelites involve the release of H_2O , into which Li partitions over minerals (Brenan et al., 1998). Lithium concentrations of metamorphic rocks therefore depend on the fraction of fluids released (F) and the Li partition coefficient between fluid and rock (${}^{\text{fluid/rock}}K_{\text{Li}} = \text{Li}_{\text{fluid}}/\text{Li}_{\text{rock}}$). Lithium partitions into metamorphic minerals found in pelites in the following order: staurolite > cordierite > biotite > muscovite > garnet (Dutrow et al., 1986). Experimental studies show that ${}^{\text{fluid/rock}}K_{\text{Li}}$ increases with temperature (Seyfried et al., 1984; Berger et al., 1988; Brenan et al., 1998; Seyfried et al., 1998). Collectively, these observations suggest that Li concentrations should decrease in metamorphic rocks with increasing metamorphic dehydration. If the process of

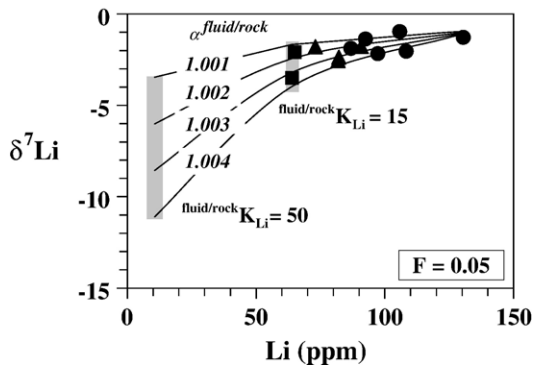


Fig. 5. Li and $\delta^7\text{Li}$ of metapelites compared with Rayleigh distillation curves calculated at variable $\alpha^{\text{fluid/rock}}$ and $\text{fluid/rock}K_{\text{Li}}$ and at constant F ; $\alpha^{\text{fluid/rock}} = \frac{[\text{Li}/\text{Li}^6/\text{Li}]_{\text{fluid}}}{[\text{Li}/\text{Li}^6/\text{Li}]_{\text{rock}}}$; $\text{fluid/rock}K_{\text{Li}} = \text{Li}_{\text{fluid}}/\text{Li}_{\text{rock}}$; F = mass fraction of fluids removed. The value for F used here (0.05) is the maximum amount of dehydration seen in the metapelites, based on LOI values. The most Li-rich chl-zone metapelite is used as the protolith. Shaded rectangles represent estimated range in $\delta^7\text{Li}$ for metapelites from the ksp zone with the lowest Li content observed (~ 65 ppm, rectangle at right), and modeled depleted metapelites with lower Li content of ~ 10 ppm (rectangle at left). The data fall between curves generated with $\alpha^{\text{fluid/rock}} = 1.001$ to 1.004.

metamorphic dehydration follows a Rayleigh distillation law, then the Li depletion correlates positively with F and $\text{fluid/rock}K_{\text{Li}}$ (Fig. 5). In order to produce the approximately two-fold depletion of Li seen in the aureole, the $\text{fluid/rock}K_{\text{Li}}$ value is estimated to be ≥ 15 assuming the maximum value of $F=0.05$ (based on LOI values) (Fig. 5).

Mineral abundances in Onawa metapelites change systematically up temperature, towards the pluton. On average, muscovite and chlorite contents decrease, cordierite content increases, while biotite content remains relatively constant (except for a clear drop in the l-v zone) (Fig. 6a). Previous studies have found that cordierite is an important Li-hosting mineral and that it can be more enriched in Li than chlorite and micas in metapelites (Dutrow et al., 1986; Cerny et al., 1997; Kalt et al., 1998). However, Li concentrations in Onawa metapelites show a strong correlation with the abundances of chlorite + muscovite + biotite + leucocratic veins (Fig. 6b) and a poor correlation with the abundances of chlorite + muscovite + biotite + total cordierite (Fig. 6c). These observations suggest that chlorite, muscovite and biotite are the main hosts of Li and that cordierite in the hornfels matrix is not so enriched in Li. The leucocratic veins dominate Li budgets in the l-v zone, likely as a result of Li incompatibility during partial melting. Cordierite may be the main host of Li in these veins, where other Li-hosting minerals do not occur. It is worth noting

that, although Li-hosting minerals exist in all metamorphic zones, Li concentrations in whole rocks still decrease with metamorphic dehydration, which reflects the fluid mobility of Li and is consistent with the estimated $\text{fluid/rock}K_{\text{Li}}$ value.

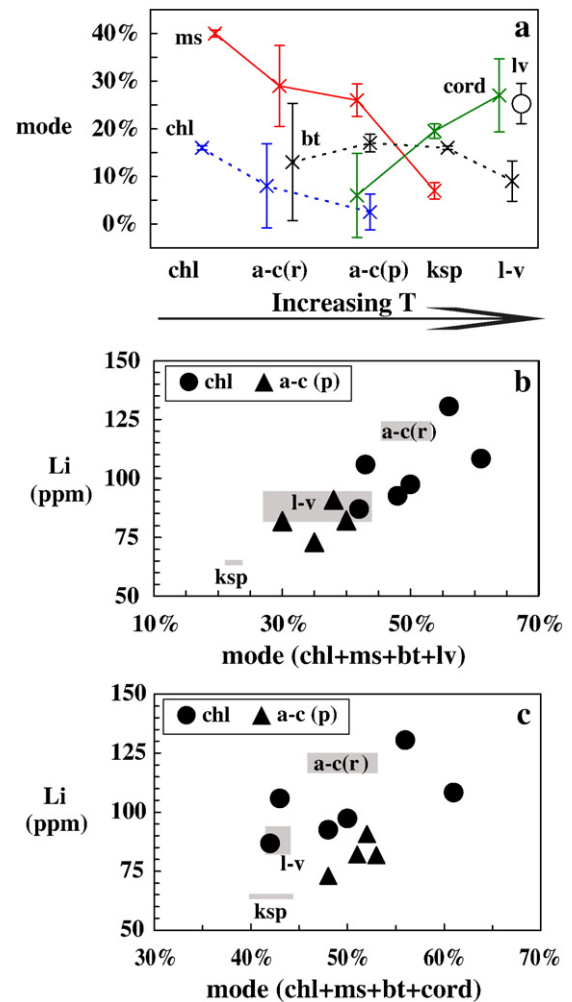


Fig. 6. Mineralogical controls on the Li content of the Onawa metapelites. a) Variation in the abundances of the dominant Li-bearing minerals in the different metamorphic zones. Chlorite disappears from the assemblage above the a-c zone and leucocratic veins only occur in the l-v zone. b) Correlation of the Li concentration with modal abundances of chl+ms+bt+l-v in different metamorphic zones; c) lack of correlation of the Li concentration with modal abundances of chl+ms+bt+total cord in different metamorphic zones. Modal mineralogy of individual samples from chl and a-c (p) zones are calculated based on the average composition of minerals (Symmes and Ferry, 1995) and whole rock composition measured here; ranges of mineral modes in l-v and a-c (r) zones are taken from Symmes and Ferry (1995) (gray rectangles); chl = chlorite; ms = muscovite; bt = biotite; cord = cordierite; l-v = leucocratic veins; Li concentration data from Table 1.

5.1.3. Limited Li isotopic fractionation during prograde contact metamorphism

Compared to the decrease of Li concentration with metamorphic dehydration, Li isotopic compositions of the metapelites show a small overall variation, with most samples falling within analytical uncertainty of one another. If this small isotopic variation results from isotopic fractionation during prograde metamorphic reactions and the progressive removal of Li can be modeled by Rayleigh distillation as an end member process, then it requires $\alpha^{\text{fluid/rock}}$ values between 1.001 and 1.004 (Fig. 5). An $\alpha^{\text{fluid/rock}}$ value so close to one indicates that Li isotopic fractionation between reactant minerals and product minerals/fluids during prograde metamorphic reactions is negligible over this temperature range. Although isotopic fractionation factors between the Li-bearing minerals in metapelites and hydrothermal fluids have not been reported, our conclusion is consistent with a recent experimental study of Li isotopic fractionation between synthetic spodumene and hydrothermal fluids. Wunder et al. (2006) report temperature-dependent Li isotopic fractionation with $\alpha^{\text{fluid/spodumene}}$ varying from 1.004 at 500 °C to ~1.001 at 900 °C (Wunder et al., 2006). This is the same range of $\alpha^{\text{fluid/rock}}$ values required to model our results (Fig. 5).

The Li isotopic compositions of samples from the leucocratic-vein zone (l-v) and retrogressed andalusite–cordierite zone (a–c (r)) indicate that the interaction with metamorphic fluids (either aqueous fluids or melts) may lead to slight but qualitatively consistent isotopic fractionation. Symmes and Ferry (1995) suggest that partial melting and vein formation in the l-v zone were driven by the up-temperature flow of H₂O-rich fluids produced by devolatilization reactions in lower-grade metapelites. Although metapelites from the l-v zone are enriched in Li relative to dehydrated rocks from the ksp zone, their Li isotopic compositions are slightly heavier than those from the ksp zone. The same relationship is observed between metapelites from prograde and retrogressed samples from the a–c zone, with the retrogressed rocks having higher Li concentration but similar or slightly higher $\delta^7\text{Li}$ values than the prograde rocks. Regardless of the origin of the fluid, the higher Li concentration in samples that interacted with fluids reflects the uptake of Li, and the Li isotopic data indicate that the fluids had a slightly heavier Li isotopic composition that was passed on to the rocks.

5.1.4. Multi-step fractionation processes during contact metamorphism?

The above discussion suggests that metamorphic dehydration produces the Li depletion observed in the

Onawa aureole and, at the same time, does not significantly fractionate Li isotopes. This is the most straightforward interpretation of the data, and is entirely consistent with recent experiments (Wunder et al., 2006). However, it is not difficult to imagine more complex scenarios for the observed lack of isotopic fractionation in the Onawa contact aureole; for example, a two-step process where metamorphic dehydration depletes Li and lowers $\delta^7\text{Li}$ in the rock, followed by fluid–rock interaction, where fluids equilibrate with isotopically light metamorphic rocks and bring their isotopic compositions back to what are observed.

While this two-step process might also explain the observations, there are problems with this interpretation. First, the petrological estimates of Symmes and Ferry (1995) and the experimental study of Wunder et al. (2006) imply that infiltration under local fluid–rock equilibrium is unlikely to be an effective agent of Li isotopic fractionation in the Onawa aureole. This, in turn, suggests that the first step of a two-step process (i.e., metamorphic dehydration) was inefficient as well. Such a two-step process (requiring minimal isotopic fractionation) differs only in detail from the model outlined in previous sections. Second, while the data from Wunder et al. (2006) argue against the possibility of large $\alpha^{\text{fluid/rock}}$ at contact metamorphic conditions, it is possible that an extremely large Li partition coefficient ($^{\text{fluid/rock}}K_{\text{Li}} \gg 15$) could have led to significant Li isotopic fractionation during dehydration. However, an isotopically enriched, Li-rich fluid is required to counteract the effects of the hypothesized dehydration-induced fractionation. Only tenuous evidence for such a fluid exists within our current sample set (e.g., in the a–c (r) samples). Lastly, the regular decrease of Li concentration with increasing grade (Fig. 4) requires that the elemental effects of dehydration are preserved throughout any process of two or more steps. That is, the infiltration-driven fractionation would have to be due to isotopic exchange almost exclusively. In order to bring the isotopically fractionated rocks back to an apparently unfractionated state, dehydration-induced fractionation and the hypothetical exchange process would have to vary regularly with grade in an equal but opposite sense.

5.2. Implications for the behavior of Li during metamorphism

Metapelites from the Onawa contact aureole were metamorphosed over a range of temperature (480 to 650 °C), lost ~75% of their original water and up to 50% of their Li, but have relatively constant $\delta^7\text{Li}$. The

implications of these results for the behavior of Li isotopes during metamorphism can be interpreted in two ways.

The metapelites experienced regional, greenschist-facies metamorphism before the intrusion of the Onawa pluton. Therefore, Li isotopic fractionation could have occurred at metamorphic grades lower than those exposed here, with the protolith having higher Li concentration and heavier isotopic compositions than what we measure. However, the high LOI, shale-like Li concentrations and isotopic composition in the chlorite-zone samples suggest that the regional metamorphism did not significantly affect Li in these metapelites. This is likely due to the small $^{fluid/rock}K_{Li}$ and F values that accompanied low-grade metamorphism, even if the $\alpha^{fluid/rock}$ value is expected to be larger at lower temperatures.

Alternatively, isotopic fractionation during metamorphism may only be manifest at greater degrees of Li loss i.e., at larger $^{fluid/rock}K_{Li}$ or F values. For example, the average Li concentration in metapelites from the ksp zone is 65 ppm and the Li isotopic composition of these samples is only $\sim 3\%$ lower than that of the chl zone. If Li concentration in these metapelites is further reduced to ~ 10 ppm, then the Li isotopic composition is expected to be much more variable and lighter than metapelites with 65 ppm Li (Fig. 5). This most likely occurs when Li-rich minerals break down to form Li-poor minerals during prograde metamorphism, resulting in a significant increase of $^{fluid/rock}K_{Li}$ values, although loss of more volatiles (increasing F) is also possible. Currently, it is difficult to test this speculation, since no Li isotopic data are available for higher-grade metapelites in the Onawa aureole that have experienced greater Li loss. Studies of mafic and intermediate granulites and alpine eclogites have clearly shown that depletion of Li is accompanied by variable and lighter isotopic compositions, when compared with their potential protoliths (Zack et al., 2003; Teng et al., 2004b).

5.3. Influence of the nature of the pluton on contact rocks

Although magmas are the sources of the heat, mass and mechanical energy that produce contact metamorphism and associated deformation (Bergantz, 1991; Labotka, 1991), the intrusion, and fluids derived therefrom, are unlikely to have directly affected the Li isotopic composition of the rocks in the Onawa contact aureole. This is because the Onawa intrusion has a lower Li concentration and heavier isotopic composition than

all metapelite samples (except for one from the retrograde a–c zone). Since Li isotopic fractionation produced during magmatic fluid exsolution is insignificant (Teng et al., 2006b), the fluids exsolved during the crystallization of the pluton should have a Li isotopic composition heavier than the metapelites. Therefore, infiltration of magmatic fluids into the contact aureole would have shifted both Li and δ^7Li of metapelites to higher values in the vicinity of the pluton, which is opposite from what we observe in the aureole (Fig. 4). Moreover, the constant major and trace element compositions within the contact aureole indicate that the effect of the Onawa pluton on the chemical composition of the aureole is small. Data from this study, therefore, highlight the importance of metamorphic reactions in controlling Li concentrations in contact metamorphic rocks, while the igneous intrusion plays a minor role, aside from its energy source.

These results are in sharp contrast with those obtained for contact halos around the Tin Mountain pegmatite, South Dakota. This Li-rich pegmatite was emplaced at a similar depth as the Onawa pluton but intruded both amphibolite and schist country rocks. The large Li concentration gradient between pegmatite and country rocks led to Li diffusion from the pegmatite into country rocks and produced a large isotopic fractionation, with both Li and δ^7Li values decreasing dramatically away from the contact into country rocks (Teng et al., 2006a). The igneous intrusion therefore controls the Li concentration and isotopic composition of country rocks at Tin Mountain, whereas the mineralogical effects of contact metamorphism induced by the pegmatite occur over a much smaller scale (Teng et al., 2006a).

Detailed comparison of these two contact environments yields the following observations: when Li in contact rocks is controlled by prograde metamorphic reactions, the isotopic fractionation is small, but the scale of Li depletion is as large as the whole contact aureole. Both Li concentrations and isotopic compositions are expected to decrease with increasing metamorphic grade towards the pluton. Alternatively, if magmatic Li dominates the Li budget in the contact environment, variations in both Li and δ^7Li can be very large, but occurs over a relatively small scale, dictated by the characteristic diffusion distance of Li. Both Li concentrations and isotopic compositions will decrease with distance from the magmatic contact, with the magnitude of variations dependent on the Li concentration gradient, the composition and permeability of the contact rocks, and temperature. Considering the markedly different interactions between country rocks and intrusions in these

two examples, Li studies could potentially be a useful tool for evaluating the mechanism of Li isotopic variation in contact aureoles and the role that the pluton plays during contact metamorphism.

6. Conclusions

Variations of Li concentration and isotopic composition during prograde metamorphism have been investigated by studying metapelites from the Onawa contact aureole. In contrast to the homogeneous major and other trace element concentrations, Li concentrations in these metapelites are depleted with increasing metamorphic grade and correlate positively with LOI and modes of chlorite + biotite + muscovite + leucocratic veins, while $\delta^7\text{Li}$ decreases only slightly. Samples that interacted with metamorphic fluids via both retrogression (a–c (r) zone) and fluid-induced melting (l–v zones) are enriched in Li but have similar or slightly heavier $\delta^7\text{Li}$ to their prograde counterparts.

The Onawa metapelites experienced contact metamorphism over temperatures of 480 to 650 °C, released large amount of fluids (e.g., LOI decreasing from 4.0 to 1.1%), experience a two-fold decrease in Li concentration, and experienced a small decrease in $\delta^7\text{Li}$ values (~3%). Rayleigh distillation modeling suggests that the fractionation factor between fluids and rocks ($\alpha^{\text{fluid/rock}}$) is between 1.000 and 1.004, consistent with minimal fractionation of Li isotopes during metamorphic dehydration at these temperatures. However, relatively large isotopic fractionation may occur for rocks that experience greater degrees of Li loss due to larger $\alpha^{\text{fluid/rock}}K_{\text{Li}}$ and F values, but such rocks are not present at Onawa. Comparison of this study with a study of Li in country rocks of Tin Mountain pegmatite illustrates the important role played by the intrusion in controlling Li in contact rocks. Lithium studies therefore could be a useful tool for evaluating the mechanism of Li concentration and isotopic variations in contact aureoles and the role that the igneous pluton plays in contact metamorphism.

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