Research paper

The behavior of lithium in amphibolite- to granulite-facies rocks of the Ivrea–Verbano Zone, NW Italy

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ABSTRACT

To investigate the behavior of Li during high-grade metamorphism and the Li composition of the lower continental crust, the Li concentrations ([Li]) and isotopic compositions (δ^7Li) of amphibolite- to granulite-facies metapelites, leucosomes and metabasites from the Ivrea–Verbano Zone, NW, Italy were determined. The average [Li] of amphibolite facies kinzigites ($79 \pm 69\ \mu g/g$, 2σ) is higher than that of granulite facies stronalites ($8 \pm 6\ \mu g/g$, 2σ) that experienced partial melting via biotite dehydration reactions. Biotite abundance and the [Li] in metapelites correlate positively, reflecting the importance of Mg-bearing phyllosilicates in controlling the Li budget of the metapelites. Despite the loss of Li following biotite breakdown, there is no significant change in δ^7Li, which averages -1.4 ± 2.0 (2σ, excluding an anomalously light sample) in the kinzigites (amphibolite facies) and $+0.9 \pm 2.9$ (2σ) in the stronalites (granulite facies). Both average δ^7Li values are comparable with those of other pelitic sediments and likely reflect the δ^7Li of their protoliths. An anomalous kinzigitic sample, with the lowest δ^7Li (-8.4) and the highest [Li] ($120\ \mu g/g$), has extremely low Ba and Sr concentrations and the highest CIA value, all indicators of a highly weathered protolith, which was likely isotopically light prior to significant metamorphism. This sample may also have experienced Li addition via diffusion, increasing [Li] and lowering δ^7Li. The leucosomes in the kinzigites and stronalites are interpreted to have formed in different ways; the former precipitated from hydrothermal fluids, have an average [Li]$= 13 \pm 2.6\ \mu g/g$ (2σ) and are isotopically similar to the kinzigites ($\delta^7Li = -1.0 \pm 0.2$, 2σ); the latter formed by dehydration melting and have lower [Li] ($3 \pm 2.6\ \mu g/g$, 2σ) that is heavier ($\delta^7Li = +6.0 \pm 6.3$, 2σ) than that of the stronalites or kinzigites. The mineralogical and compositional characteristics of the stronalites are consistent with substantial Li loss during partial melting. A melting model indicates that Li removed from the stronalites may contribute to the formation of S-type granites or Li-enriched pegmatites.

Three granulite-facies metabasites have relatively constant [Li] of 3.0–4.2 μg/g (average 3.6 ± 1.2, 2σ) and variable δ^7Li of -3.2 to $+3.3$ (average 0 ± 6.5, 2σ). While these concentrations are typical of those of possible basaltic protoliths, the highly variable δ^7Li suggests Li mobility during metamorphism. Collectively, the Li signatures in granulite facies stronalites and metabasites indicate the [Li] of this section of lower continental crust is close to 8 μg/g or less, and the concentration weighted δ^7Li of this section of the lower continental crust is $+1.0$, which is similar to a previous estimate (8 μg/g, $+2.5$).

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1. Introduction

Since the original work of Zack et al. (2003) on Li fractionation in eclogites, several studies have focused on the behavior of Li during metamorphic dehydration (e.g., Marschall et al., 2007; Teng et al., 2007) in order to understand the distribution of Li concentrations ([Li]) and isotopic compositions (δ^7Li, $\delta^7Li = [(^7Li/^6Li)_{sample}/(^7Li/^6Li)_{LSVEC} - 1] \times 1000$) during crustal recycling at subduction zones (e.g., Elliott et al., 2004; Tomascak, 2004; Elliott et al., 2006). The consensus of these latter studies is that metamorphic dehydration has had only a subtle influence on δ^7Li in rocks metamorphosed at amphibolite or eclogite facies. Likewise, our recent studies have shown that, although Li depletion may occur during sub-greenschist to greenschist facies metamorphic dehydration, Li isotopic fractionation is indiscernible (Qiu et al., 2009, 2011). Rather, the [Li] and δ^7Li of low grade metapelites correlate with the weathering intensity experienced in the sedimentary provenance, as reflected by indicators such as the Chemical Index of Alteration (CIA); [Li] generally increases and δ^7Li values typically decrease with increasing weathering intensity (Qiu et al., 2009, 2011). Despite recent progress in understanding the geochemical behavior of Li during low- to intermediate-grade metamorphism, the behavior of Li during high-grade (amphibolite to granulite facies) metamorphic

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devolatilization, which is accompanied by partial melting and migmatization processes, has not been investigated.

Regional granulite facies metamorphism in OH-bearing rocks, such as pelites, is generally envisaged as causing the dehydration of the protolith, and the release of fluids can subsequently affect element distributions in crustal rocks. Previous geochemical studies of the metapelites from the Ivrea–Verbano Zone, NW Italy (e.g., Sighinolfi and Gorgoni, 1978; Schnetger, 1994; Bea and Montero, 1999), have suggested that granulite facies metamorphism, initiated by the intrusion of mantle-derived magma, resulted in significant depletion of fluid-mobile elements in the metapelites. The depletion of Li and other fluid-mobile elements (e.g., K, Rb, Sr, and Cs) has been used to mark the transition from amphibolite to granulite facies metamorphism (Sighinolfi and Gorgoni, 1978; Schnetger, 1994). Among these elements, Li is depleted by the greatest amount, with 80% to 98% being lost in the granulite facies rocks (Sighinolfi and Gorgoni, 1978; Schnetger, 1994; Bea and Montero, 1999). These results indicate strong partitioning of Li into the fluids/melts liberated by granulite facies metamorphic dehydration and partial melting reactions. Thus, the Li signatures in granulite-facies metapelites from the Ivrea–Verbano Zone can provide important information about the behavior of Li during high-grade metamorphism.

These granulite-facies samples also supply a means to investigate the Li composition of the lower continental crust, since granulite-facies metamorphic terranes are one of the two types of samples (the other is granulite-facies xenoliths) that have been used to study the composition of lower continental crust (e.g., Rudnick and Presper, 1990; Rudnick and Fountain, 1995). Estimates of the Li concentration in the lower continental crust (6 to 14 µg/g) have been made based on studies of high grade metamorphic terranes and granulite xenoliths (Taylor and McLennan, 1985; Shaw et al., 1994; Rudnick and Fountain, 1995; Wedepohl, 1995; Rudnick and Gao, 2003; Teng et al., 2008); however, the Li isotopic composition of lower continental crust is still poorly

constrained. By studying three suites of granulite-facies xenoliths from China and Australia, Teng et al. (2008) found the lower crust to be strongly heterogeneous in δ^7Li, with δ^7Li of individual samples ranging from −14 to +14.3, with a concentration weighted average of +2.5.

In order to understand the behavior of Li during high-grade metamorphic devolatilization and partial melting, and place further constraints on [Li] and δ^7Li of lower continental crust, previously well-characterized samples from the Ivrea–Verbano Zone are investigated here.

2. Geological setting and samples

The Ivrea–Verbano Zone is a SW–NE-striking section of Paleozoic basement exposed in the Southern Alps in northern Italy, which is ~15 km in width and 120 km in length, bordered by the Insubric Line to the NW and by the Strona–Ceneri Zone to the SE (Fig. 1). The Ivrea–Verbano Zone contains three major lithologies: 1) supracrustal rocks (traditionally called the Kinzigite Formation), 2) mantle peridotites, and, 3) a mafic complex. The Mafic Complex formed by intrusion of basaltic magma into the lower crust, and is commonly considered as the heat source for the regional metamorphism observed in the Kinzigite Formation, ca. 270–290 Ma (Voshage et al., 1990; Barboza and Bergantz, 2000 and references therein); it comprises the base of the Ivrea–Verbano Zone and consists of a variety of gabbros and diorites metamorphosed up to the granulite facies. The Kinzigite Formation comprises middle amphibolite- to granulite-facies, migmatized metapelites and metapsammite (metamorphic sandstones) with minor intercalations of metabasites (metamorphosed gabbros or diorites of the Mafic Complex) and quartzites (Zingg, 1984). The lowest grade metapelites of the Kinzigite Formation are mica schists. With increasing metamorphic grade, these lithologies evolve into garnet- and sillimanite-bearing schists called kinzigites. The biotite in this prograde sequence is progressively replaced by garnet, until
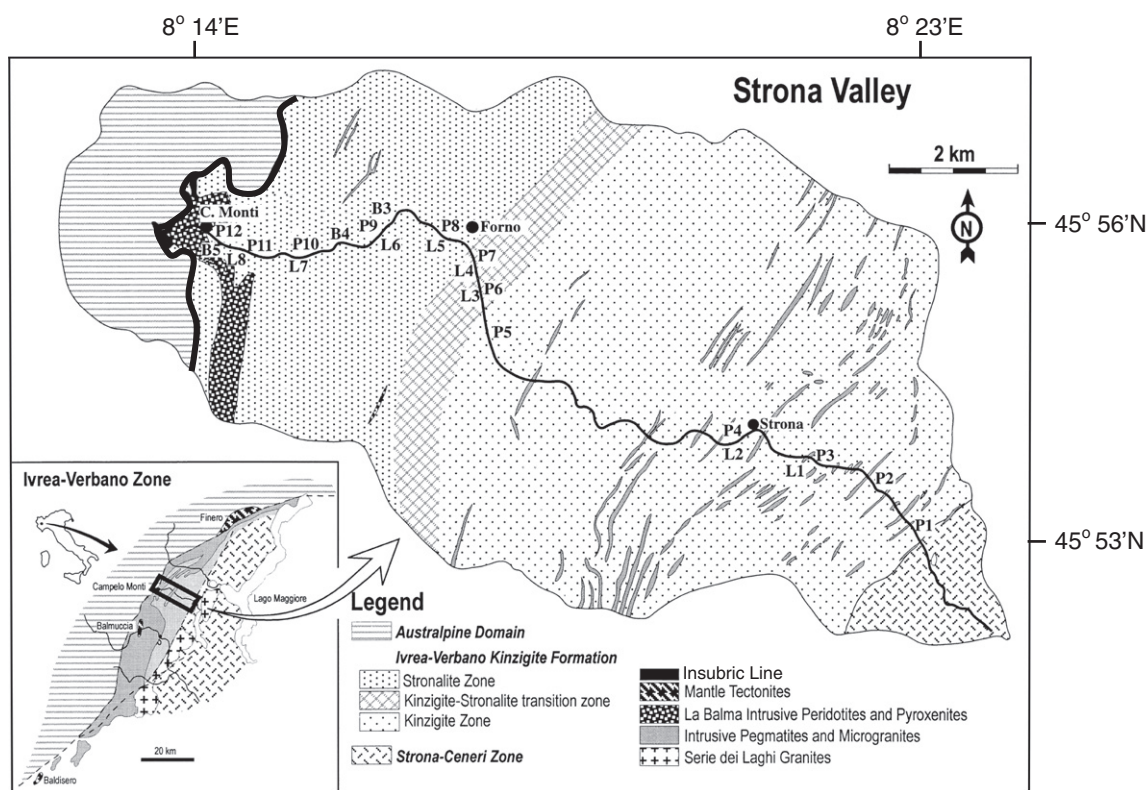

Fig. 1. Sketch map showing the location of Ivrea–Verbano zone, NW, Italy (from Bea and Montero, 1999). Metabasites of the Mafic Complex are intercalated with the Kinzigite Formation and are not explicitly indicated on this map. Labels indicate samples mentioned in Tables 1–3.

biotite is completely replaced by garnet in granulite-facies metapelites, which are locally called stronalites (Bertolani and Garuti, 1970; Luvizotto and Zack, 2009). In addition, one kinzigite sample, P1, contains >5 cm-thick quartz veins and is the only kinzigite in our study to contain such veins; the quartz veins of P1 were separated out completely during the sample preparation. The granulite-facies metabasites, which are intercalated with the stronalites, are migmatized and composed of brown hornblende, clinopyroxene, orthopyroxene and plagioclase, with accessory opaques, rutiles and apatite (Mazzucchelli and Siena, 1986).

In this study, following Bea and Montero (1999), the prograde metapelitic sequence along the Strona Valley (Fig. 1) is divided into three zones: the kinzigite, transition and stronalite zones, having modal biotite/garnet >2, between 0.5 and 2, and <0.5, respectively, and peak metamorphic pressures of roughly 0.4–0.5 GPa, 0.5–0.6 GPa, and 0.6–0.8 GPa, respectively. Leucosomes, the formation of which are related to the dehydration melting of biotite, are widespread in the stronalite zone and occur as dikes or lenses of different sizes, all with compositions similar to that of a garnet-bearing leucogranite or leucogranodiorite. In contrast, leucosomes are less abundant in the transition zone and upper kinzigite zone, where they are interpreted to derive from partial melting associated with muscovite breakdown (Bea and Montero, 1999, and references therein). Generally, the leucosomes are composed of quartz + plagioclase + K-feldspar ± garnet.

The modal mineralogy, based on point counting, and estimated P–T of the 12 metapelites investigated here are reported in Table 1 (Bea and Montero, 1999). Additionally, seven leucosome samples were collected from the kinzigite zone, transition zone and stronalite zone along the Strona Valley, and three granulite-facies metabasites were collected from the stronalite zone; their compositions are reported in Tables 3 and 2, respectively.

Most of the whole rock powders analyzed in this study have previously been analyzed for major and trace elements by Bea and Montero (1999). Two powders (P7 and P12) analyzed in our study were obtained by re-crushing the hand specimens because the original powders were exhausted. Additionally, the [Li] of two samples (P6 and L7) are taken from Bea and Montero (1999) since the original powders and specimens are both exhausted, and therefore the Li isotopic compositions of these samples are not reported.

3. Analytical methods

Lithium concentrations and isotopic compositions of the metapelites, leucosomes and metabasites collected for this study were determined at the Geochemistry Laboratory of the University of Maryland, College Park. Sample dissolution procedures, column chemistry, instrumental analysis and external precision are reported in Teng et al. (2006b) and Qiu et al. (2009).

Briefly, samples were dissolved in screw-top Teflon beakers with a combination of HF–HNO_3–HCl. Lithium was purified on a cation exchange resin (Bio-Rad AG50w-X12, 200–400 mesh) first in an HCl medium, followed by an HCl–ethanol medium. The final Li solutions are introduced into the Nu Plasma MC-ICPMS by an auto-sampler (ASX-100® Cetac Technologies) through a desolvating nebulizer, either Aridus® Cetac Technologies fitted with a PFA spray chamber and micronebulizer or Apex-IR with 2 PFA micro-flow nebulizers (Elemental Scientific Inc.). The solutions usually have ~50 ng/g Li and the uptake rate of the solution is 30 to 50 μl/m. The ^7Li and ^6Li are measured simultaneously in two Faraday cups, H6 and L5, respectively. The typical voltage on the measurements of Li in a 50 ppb solution is ~2 V on ^7Li (20 pA on $10^{11} \Omega$ resistor), which works out to ~0.003% transmission efficiency; for comparison, the blank of Li is about 10 mV on mass 7. Lithium concentrations and isotopic compositions were analyzed using the standard-sample-bracketing method. The long-term external precisions of the Li isotopic composition and concentration analyses are ≤1.0‰ (2σ) and ±10% (2σ), respectively, based on repeat analyses of pure Li standards and standard reference materials, respectively, over the past nine years (Rudnick et al., 2004; Teng et al., 2006b; Qiu et al., 2011). Qiu et al. (2009, 2011) reported results for three separate analyses of BCR-1 [δ^7Li = +2.1 ± 0.3 and [Li] = 12.7 ± 0.7 μg/g], which were analyzed during the course of this study; in comparison, Magna et al. (2004), Rudnick et al. (2004) and Teng et al. (2006b), reported the δ^7Li of BCR-1 to be +2.0 ± 0.7 (10 runs), δ^7Li = +2.7 ± 1 (3 runs) and δ^7Li = +2.4 ± 0.5 (4 runs), respectively, and the GEOREM (Jochum and Nohl, 2008) preferred BCR-1 [Li] = 13 ± 1 μg/g.

4. Results

Lithium concentrations and isotopic compositions of the metapelites, metabasites and leucosomes analyzed here are reported in Tables 2 and 3, along with the previously published major and trace element concentrations from Bea and Montero (1999).

The [Li] determined in this study are generally within 2σ analytical uncertainties of those determined by Bea and Montero (1999) via PE SCIEX ELAN-5000 spectrometer (Tables 2 and 3 and Appendix A). Exceptions are samples with [Li]<20 μg/g (P9, P10, P12, L1, L2, L5,L11, B4 and B5); the [Li] of these samples determined by Bea and Montero

Table 1
Modal composition and geothermobarometric estimates for metapelites from the Strona Valley section, which is nearly perpendicular to metamorphic gradient. Values are from Bea and Montero (1999).

	Kinzigites					Transition		Stronalites				
Sample no.	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
Estimated PT conditions												
P^{Gasp} (GPa)	0.40	0.42	0.43	0.45	0.50	0.55	0.60	0.63	0.70	0.73	0.78	0.80
T^{bi-gar} (°C)	500	560	560	600	630	670	700	750	750	≈800	≈800	≈800
Modal composition (wt.%)												
Orthopyroxene	n/a	n/a	n/a	n/a	n/a	n/a	n/a	7.2	n/a	n/a	n/a	n/a
Cordierite	2.6	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Biotite	25.6	21.9	20.2	44.1	22.2	15.4	14.8	2.8	5.1	4.1	0	0.3
Garnet	0.0	1.5	1.7	1.3	5.1	16.1	19.3	15.3	28.8	35.1	48.6	53.6
Sillimanite	10.8	3.8	5.0	10.2	1.0	6.8	5.6	10.3	19.3	14.3	29.0	31.4
Quartz	49.5	51.6	46.3	28.9	33.0	34.6	28.6	34.7	26.8	17.7	13.4	8.9
K-feldspar	1.3	2.7	2.9	1.6	0.7	12.8	10.7	11.9	14.8	15	6.4	1.9
Plagioclase	9.0	17.3	23.0	11.0	37.5	13.4	20.3	16.8	3.9	12.1	1.1	3.4
Apatite	0.31	0.3	0.37	0.31	0.35	0.22	0.07	0.1	0.05	0.09	0.03	0.008
Monazite	0.037	0.018	0.026	0.032	0.03	0.021	0.029	0.024	0.024	0.053	0.041	0.036
Xenotime	0.003	0.002	0.001	0.001	0.001	0.0005	n/a	n/a	n/a	n/a	n/a	n/a
Zircon	0.051	0.022	0.038	0.043	0.038	0.049	0.048	0.048	0.044	0.038	0.054	0.062
Others*	0.80	0.85	0.50	2.50	0.20	0.60	0.65	0.90	1.20	1.60	1.40	0.50

* ilmenite + rutile + graphite + sulfides.

Table 2
Lithium concentrations (μg/g), Li isotopic compositions (δ^7Li), major (wt.%) and trace element concentrations (μg/g) of metapelites from the Strona Valley. Values of major and other trace elements are from Bea and Montero (1999).

Sample no.	Kinzigites					Transition		Stronalites					Metabasites		
	P1	P2	P3	P4	P5	P6	P7*	P8	P9	P10	P11	P12*	B3	B4	B5
δ^7Li	−8.5	−1.8	−0.1	−1.5	−2.4	n/a	0.4	2.1	−0.2	−1.1	1.8	1.8	3.3	0.0	-3.2
Li	120	58	60	113	46	n/a	42	10.8	5.2	6.3	11.1	4.6	4.2	3.6	3.0
Li [a]	122	55	63	107	49	39	42	12	9	9	12	8	4	7	7
SiO_2	70.4	73.9	72.9	56.8	63.9	64.9	63.9	59.2	58.1	56.7	41.8	45.0	45.8	48.6	50.8
TiO_2	0.71	0.78	0.73	1.28	0.85	0.77	0.88	1.45	1.42	1.54	2.09	1.95	2.21	1.71	1.76
Al_2O_3	15.8	12.7	13.0	21.5	16.3	16.1	16.8	22.1	22.6	22.3	30.0	30.1	12.2	20.0	14.5
FeO total	3.70	4.95	4.47	8.68	5.83	7.65	7.35	10.11	10.22	9.83	15.25	13.67	12.73	10.48	10.28
MgO	4.89	1.86	2.62	3.33	3.04	2.74	3.79	3.34	3.43	3.40	5.57	5.06	13.53	4.70	7.46
MnO	0.03	0.09	0.06	0.13	0.10	0.12	0.10	0.11	0.10	0.10	0.28	0.12	0.20	0.20	0.18
CaO	0.29	0.82	1.15	0.77	4.43	1.53	1.58	0.45	0.33	0.75	1.36	0.69	10.92	9.67	11.5
Na_2O	0.28	1.14	2.45	1.02	1.87	0.95	1.72	0.53	0.43	1.38	0.79	0.75	0.90	2.79	0.52
K_2O	2.62	2.30	1.94	4.40	2.12	3.47	3.32	2.09	2.98	3.01	1.18	1.81	0.07	0.28	0.05
P_2O_5	0.15	0.16	0.18	0.15	0.18	0.14	0.03	0.06	0.06	0.08	0.06	0.02	0.02	0.33	0.22
L.O.I.	1.05	0.71	0.87	1.40	0.92	1.03	0.57	0.48	0.09	0.68	0.79	0.38	0.44	0.82	1.79
Total	99.8	99.4	100.3	99.5	99.6	99.5	100.0	99.9	99.7	99.7	99.1	99.5	99.1	99.6	99.0
CIA	82	70	62	74	56	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Rb	64	112	80	203	87	75	81	16	35	44	21	12	1.2	1.6	1.7
Cs	1.8	5.5	1.5	11	4.1	0.2	0.3	0.3	0.2	0.3	0.3	0.2	0.1	0.3	0.1
Be	1.7	1.9	1.3	3.9	2.9	1.6	1.7	0.3	0.3	0.3	0.6	0.9	0.3	1.3	2.5
Sr	15	125	134	103	177	189	172	81	95	160	129	61	157	422	180
Ba	183	509	554	626	608	621	589	356	427	717	411	387	24	116	72
Sc	10	10	12	21	15	20	18	19	21	26	44	35	44	43	39
V	81	65	87	151	106	127	104	177	171	183	280	220	389	239	273
Cr	66	57	76	159	67	133	109	193	186	118	222	240	686	5.5	576
Ni	37	30	32	62	40	56	43	99	59	85	78	65	268	15	162
Cu	5.0	8.0	27	33	138	5	7	14	13	52	24	7.0	71	18	18
Zn	36	63	36	147	81	38	47	128	108	120	183	131	135	109	151
Ga	22	17	15	33	22	21	23	30	30	30	42	42	17	24	20
Y	22	11	13	14	33	30	27	22	31	34	60	66	27	40	40
Nb	18	15	10	22	13	19	22	18	17	18	37	43	1.7	8.8	12
Ta	1.5	1.2	0.8	1.7	1.2	1.7	1.9	0.9	0.9	1.0	2.0	2.2	0.1	0.5	1.1
Zr	339	136	211	255	204	293	280	275	264	220	327	394	56	120	107
Tl	0.4	0.6	0.4	1.2	0.6	0.4	0.4	0.3	0.5	0.4	0.2	0.1	0.0	0.0	0.0
Pb	2.5	20	4.3	18	15	17	21	12	13	9.3	5.5	5.3	1.1	2.8	4.3
U	2.6	1.4	1.6	2.8	3.0	2.0	2.0	0.6	0.8	1.5	1.0	1.0	0.0	0.0	0.2
Th	14	8.2	10	16	16	11	12	8.8	13	21	15	15	0.1	0.0	0.8
La	46	30	33	53	50	40	42	26	34	63	52	45	1.4	11	15
Ce	94	65	69	114	98	84	89	58	74	126	101	93	6.4	28	38
Pr	11	7.3	7.8	13	11	10	10	6.8	9.2	14	12	10	1.4	4.5	5.6
Nd	39	27	29	48	42	27	33	25	35	55	45	41	9.2	22	25
Sm	6.9	5.5	6.0	9.6	7.9	5.7	6.2	5.3	7.4	9.6	8.7	8.6	3.5	6.6	7.0
Eu	1.1	1.4	1.5	1.8	1.6	1.3	1.3	1.2	1.7	1.8	1.3	1.2	1.1	2.5	2.1
Gd	6.2	5.5	5.6	9.0	6.8	5.6	6.3	5.3	6.9	7.5	10.1	7.6	4.3	6.5	6.7
Tb	0.9	0.6	0.7	0.9	1.0	0.8	0.9	0.7	1.0	1.1	1.7	1.5	0.8	1.1	1.1
Dy	4.7	2.4	2.9	3.5	5.7	5.1	5.0	4.1	5.7	6.3	10.8	10.6	4.7	6.8	6.8
Ho	0.9	0.4	0.5	0.5	1.2	1.1	1.0	0.9	1.2	1.4	2.4	2.5	1.0	1.5	1.4
Er	2.1	1.0	1.3	1.3	3.2	3.1	2.8	2.5	3.4	3.6	6.4	7.3	2.8	4.0	3.9
Tm	0.3	0.2	0.2	0.2	0.5	0.5	0.5	0.4	0.5	0.6	1.0	1.2	0.4	0.6	0.6
Yb	1.8	1.0	1.1	1.1	3.1	3.1	3.3	2.7	3.6	3.7	6.5	7.5	2.5	3.6	3.7
Lu	0.24	0.14	0.16	0.15	0.44	0.48	0.47	0.40	0.53	0.53	0.94	1.19	0.34	0.53	0.55
Nb/Ta	12.0	12.5	13.1	12.9	10.8	11.1	11.5	18.9	17.3	18.0	18.5	19.5	7.4	17.7	11.3
Nd/Th	2.7	3.3	2.8	3.0	2.7	2.5	2.7	2.9	2.7	2.6	2.9	2.7	92	555	33
Th/U	5.5	6.0	6.3	5.6	5.3	5.3	6.1	14.6	15.5	13.9	14.8	14.5	4.5	4.0	3.2

At least two aliquots (~25 mg each) of each sample were digested and put through the column chemistry procedures.
The Li data reported in this study represent the averages of ≥4 measurements of each sample.
The uncertainties for [Li] (mg/g) and δ^7Li are ± 10 (2σ) and ± 1 (2σ), respectively.
CIA = $Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)$ x100 (molar contents, with CaO^* being CaO content in silicate fraction of the sample).
[a] : Li concentrations from Bea and Montero (1999), analyzed by PE SCIEX ELAN-5000 spectrometer.
* : powders for these samples are from re-crushing the same handsamples used in Bea and Montero (1999).

(1999) are generally 10–50% higher than the value determined in this study. However, since the [Li] between low- and high-grade metapelites differ by about two orders of magnitude (a few μg/g to hundreds of μg/g), the discrepancy in [Li] of the metapelites between the two studies (less than one order of magnitude) will not influence the discussion and conclusions related to the metamorphic effects. Additionally, the average [Li] of granulite-facies samples (stronalites and metabasites) between the two studies generally overlap, considering the 2σ uncertainties; therefore, the discrepancy has only a minor influence on the estimates of [Li] in the lower continental crust. We also report both the arithmetic and

log-normal mean of [Li] in kinzigite, transition, stronalite, leucosomes and metabasite samples in Table 4. The arithmetic and log-normal mean are similar, reflecting the normal distribution of the data; we use the arithmetic mean for comparisons of the data.

Lithium concentrations in the metapelites vary widely (Tables 2 and 4 and Figs. 2 and 3a), from a low of 5, up to 120 μg/g; kinzigites have significantly higher concentrations (46–120 μg/g, average 79 ± 69 μg/g, 2σ) than samples from the transition zone (39–42 μg/g, average 41 ± 8 μg/g, 2σ) and the stronalite zone (5–11 μg/g, average 8 ± 6 μg/g, 2σ). Previous studies have reported average [Li] for kinzigite zone

Table 3
Lithium concentrations (µg/g), Li isotopic compositions, major (wt.%) and other trace elements (µg/g) of leucosomes from the Strona Valley. Major and trace element data are from Bea and Montero (1999).

Sample no.	Kinzigites		Transition		Stronalites		
	L1	L2	L3	L4	L5	L7	L8
$\delta^7 Li$	−1.0	−0.9	7.5	3.3	3.7	n/a	8.2
Li	14.7	12.1	7.7	5.6	4.6	n/a	2.6
Li [a]	18	18	8.1	6.2	8.4	3.2	2.4
SiO_2	78.4	79.7	76.4	73.1	72.4	71.5	74.7
TiO_2	0.15	0.05	0.02	0.04	0.39	0.38	0.18
Al_2O_3	12.6	12.1	13.2	14.9	14.5	15.1	13.7
FeO^{total}	0.97	0.28	0.55	0.79	2.77	2.51	1.71
MgO	0.38	0.2	0.12	0.21	0.91	0.81	0.36
MnO	0.02	0.01	0.04	0.04	0.06	0.04	0.04
CaO	1.81	1.90	1.50	0.82	1.52	1.39	1.06
Na_2O	3.13	4.58	2.14	2.16	2.27	2.41	3.10
K_2O	1.53	0.20	5.78	7.42	5.18	5.41	4.52
P_2O_5	0.15	0.24	0.05	0.02	0.11	0.12	0.13
L.O.I.	0.7	0.33	0.12	0.35	0.09	0.24	0.1
Total	99.8	99.5	99.9	99.9	100.1	99.9	99.7
Rb	45	3.7	120	167	95	110	153
Cs	0.9	0.04	0.97	1.9	0.06	0.25	0.1
Be	2.8	1.4	1.4	1.5	0.26	0.62	0.53
Sr	323	221	225	207	161	165	67
Ba	993	104	496	1010	723	659	344
Sc	2.4	1.1	1.4	1.9	7.1	7.6	3.5
V	16	2.8	0.9	1.6	34	19	12
Cr	0.3	2.8	5.4	1.4	0.5	1.0	7.7
Ni	1.7	4.7	4.2	0.5	0.0	13	3.3
Cu	4.8	4.1	1.9	1.2	2.2	3.7	2.4
Zn	26	6.0	8.0	23	20	42	21
Ga	9.6	7.1	10	11	15	14	17
Y	9.9	7.6	6.5	2.7	55	9.6	21
Nb	2.2	0.88	0.19	0.26	4.1	4.1	5.3
Ta	0.49	0.26	0.03	0.08	0.3	0.89	0.52
Zr	24	6.0	66	46	166	83	92
Tl	0.19	0.02	0.63	0.91	0.49	0.60	0.80
Pb	50	8.8	65	60	29	45	21
U	0.44	0.26	0.31	0.42	0.42	0.33	0.44
Th	1.9	0.27	0.23	0.90	9.0	5.3	4.2
La	9.2	1.3	2.1	1.9	25.6	17.3	10.9
Ce	18	3.0	4.3	3.9	64	42	26
Pr	2.1	0.4	0.4	0.4	6.3	4.5	2.9
Nd	7.8	1.9	1.3	1.6	23	15	11
Sm	1.7	0.66	0.26	0.32	5.5	3.8	2.6
Eu	2.7	0.67	0.71	0.58	0.95	0.77	0.44
Gd	1.8	0.87	0.31	0.30	6.0	3.7	2.9
Tb	0.28	0.17	0.10	0.07	1.0	0.45	0.55
Dy	1.7	1.1	1.0	0.62	7.5	2.1	3.7
Ho	0.35	0.24	0.30	0.16	1.9	0.38	0.75
Er	0.97	0.67	0.98	0.49	6.2	0.94	1.9
Tm	0.15	0.11	0.16	0.08	1.1	0.14	0.28
Yb	0.87	0.66	0.89	0.47	6.7	0.86	1.72
Lu	0.12	0.09	0.13	0.07	0.94	0.13	0.23
Nb/Ta	4.4	3.3	5.4	3.3	13.8	4.6	10.1
Nd/Th	4.0	7.0	5.4	1.8	2.6	2.8	2.5
Th/U	4.4	1.0	0.7	2.1	21	16	9.6

a: Li concentrations from Bea and Montero (1999).
At least two aliquots (~25 mg each) of each sample were digested and put through the column chemistry.
The Li data reported in this study represent the averages of ≥4 measurements of each sample.
The uncertainties for [Li] (µg/g) and δ7Li are ± 10 (2σ) and ± 1 (2σ), respectively.

metapelites between 103 µg/g (Sighinolfi and Gorgoni, 1978) and 57 µg/ g (Schnetger, 1994). Previously reported average [Li] of stronalite zone samples are 15 µg/g (Sighinolfi and Gorgoni, 1978) and 14 µg/g (Schnetger, 1994); these values are generally at the higher end of 2 σ uncertainty of the average [Li] determined in our study. The [Li] of three granulite-facies metabasites is systematically lower than that of stronalites (3.0 to 4.2 µg/g versus 4.6 to 11 µg/g, respectively).

The leucosomes analyzed here exhibit a relatively limited range in [Li] (3–15 µg/g, Tables 2 and 4 and Fig. 3a), with leucosomes from the

Table 4
Comparison of Li concentration (µg/g) of metapelites and leucosomes between different studies. a is from this study, b is from Schnetger (1994), and c is from Sighinolfi and Gorgoni (1978).

From	Kinzigites			Transition	Stronalites			Leucosomes	Metabasites
	a	b	c	a	a	b	c	a	a
N.	5	14	38	2	5	46	33	7	3
Max.	120	81	n/a	42	11	70	n/a	15	4.2
Min.	46	16	n/a	39	5	2	n/a	3	3.0
Mean	79	57	103	41	8	14	15	7	3.6
Mean (LN.)	74			41	7			6	3.7

N.: the number of total samples
LN.: lognormal.

kinzigite zone (12–15 µg/g) characterized by higher concentrations than those from the transition zone (6–8 µg/g) and stronalite zone (3–5 µg/g).

Lithium isotopic compositions of metapelites from the kinzigite zone (Figs. 2 and 3b) show a large range (δ⁷Li of −8.5 to −0.1) relative to samples from higher metamorphic grade; the $\delta^7 Li$ of one anomalously light sample (P1, $\delta^7 Li = -8.5$) is not included in the average $\delta^7 Li$ of kinzigites, since it is a statistical outlier (plotting outside of the "outer fence", defined by 3× the interquartile range). This sample's unusual composition is discussed in Section 5.2. The average $\delta^7 Li$ of kinzigites, $\delta^7 Li = -1.4 \pm 2.0$ (2σ), is indistinguishable from that of the transition ($\delta^7 Li = +0.4$) and stronalite (average $= +0.9 \pm 2.9$, 2σ) zones. The $\delta^7 Li$ values of the leucosomes get progressively heavier from the kinzigite (−0.9 to −1, average $\delta^7 Li = -1.0 \pm 0.2$, 2σ) to transition (+3.3 to +7.5, average $\delta^7 Li = +5.4 \pm 6.0$, 2σ) to stronalite ($\delta^7 Li = +6.0 \pm 3.2$, 1σ) zones (Fig. 3b). The granulite metabasites have $\delta^7 Li$ of −3.2 to +3.3 (average 0 ± 6.5, 2σ), which overlap those of the stronalites.

5. Discussion

5.1. Factors controlling the [Li] of metapelites

Recent studies have concluded that Li in metamorphic rocks can be depleted by 20–50% during greenschist to lower amphibolite facies (250 to 650 °C) metamorphic dehydration (e.g., Zack et al., 2003; Marschall et al., 2007; Teng et al., 2007; Qiu et al., 2011). These results are consistent with Li being a fluid-mobile element having a rock–fluid partition coefficient ($^{rock/fluid}D_{Li}$) that negatively correlates with
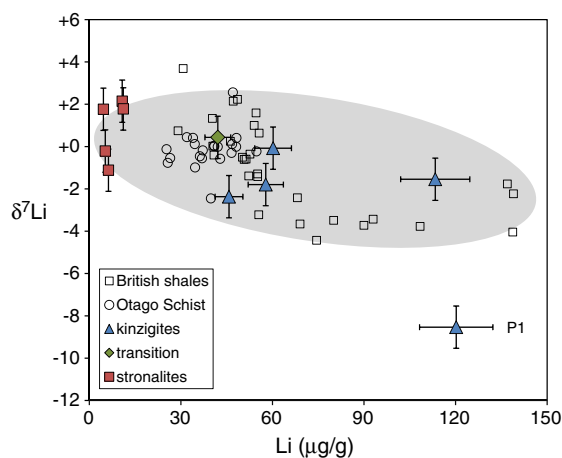

Fig. 2. Plot of δ⁷Li versus [Li] for metapelites from the three zones. Error bars indicate the 2σ uncertainty of Li isotopic compositions (±1‰) and 2σ uncertainties of Li concentrations (±10%). British shales and Otago Schist data are from Qiu et al. (2009) and Qiu et al. (2011), respectively. Sample P1 has different Li signature from the other metapelites, the latter of which are marked by the gray cloud.
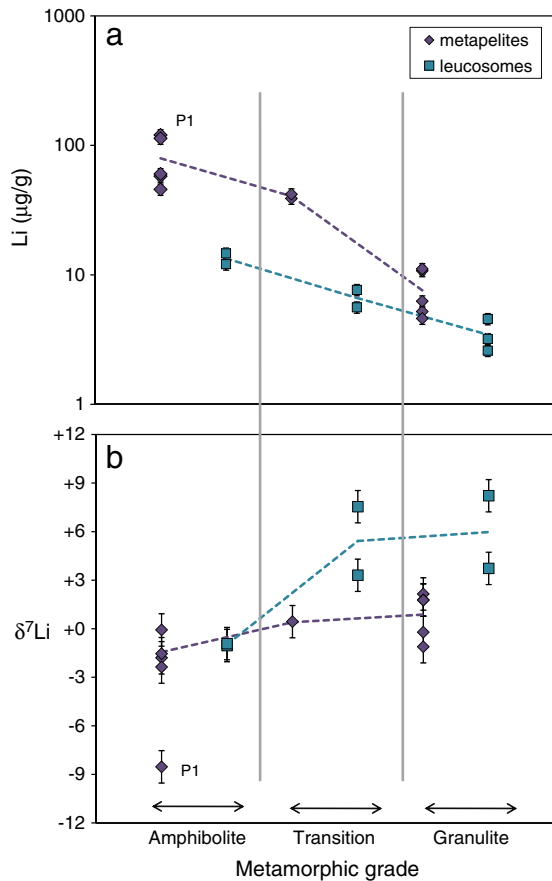
Fig. 3. Plot of Li concentrations (a) and Li isotopic compositions (b) versus metamorphic grade for the metapelites and leucosomes from the three zones. Note: y-axis of (a) is logarithmic. The dashed purple and green lines connect the average value of [Li] and δ^7Li in metapelites and leucosomes of three zones, respectively. Error bars indicate 2σ uncertainty. The vertical gray bars are indicative of the transition of metamorphic grade.

temperature (Seyfried et al., 1998). From amphibolite to granulite facies (i.e., kinzigites to stronalties), the [Li] of Ivrea–Verbano Zone metapelites are depleted by up to ~90% (Figs. 2 and 3a), suggesting
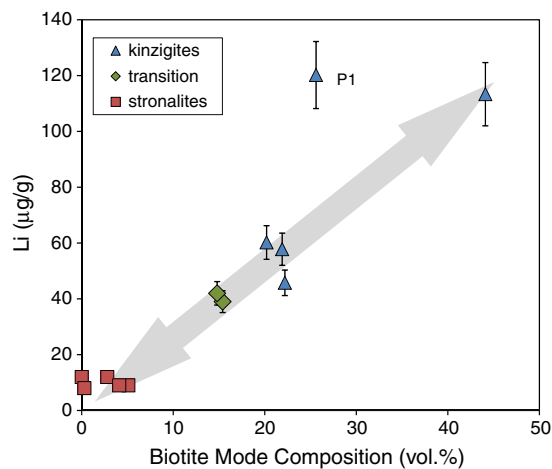
that dehydration-related partial melting significantly contributes to the depletion of Li in metapelitic granulites.

The positive correlation between [Li] and biotite abundance (Fig. 4), which is not found for any other mineral, suggests that biotite is the main host of [Li] in kinzigite and stronalite rocks (Hezel et al., 2011). The breakdown of biotite during partial melting occurs through the reaction (Schnetger, 1994; Luvizotto and Zack, 2009):

biotite + sillimanite + plagioclase + quartz→K−feldspar + garnet + rutile + melt

Consumption of biotite releases Li and, if this Li is not significantly partitioned into any other mineral in the rock, then large amounts of Li are lost with the melt; as a result, the stronalites are significantly depleted in Li relative to the kinzigites. The protolith of the metapelites experienced other dehydration reactions prior to biotite breakdown in the Ivrea–Verbano Zone. One such major reaction is muscovite breakdown (Sighinolfi and Gorgoni, 1978):

muscovite + quartz→sillimanite + K−feldspar + H$_2$O

during the formation of kinzigites.

Thus, we wish to determine whether [Li] in the kinzigites reflects the net result of a series of dehydration reactions from diagenesis to amphibolite facies metamorphism; if Li is released during dehydration, the [Li] in kinzigites should be lower than that of their pelitic protolith. We note, however, that the average [Li] of the kinzigites (79 ± 69 μg/g, 2σ) is within the range of PAAS (Post Archean Australian Shales, Nance and Taylor, 1976; average 63 ± 50 μg/g, 2σ, Teng et al., 2004) and other pelitic sediments (Chan et al., 2006) and sedimentary rocks (Qiu et al., 2009), which are considered representative of typical pelitic sediments. Notably, the [Li] of two kinzigites is as high as the most Li-enriched pelitic sediments found in British shales (Fig. 2, [Li]>100 μg/g, Qiu et al., 2009) and all kinzigites plot on the correlation between [Li] and weathering intensities (Chemical Index of Alteration, CIA, Nesbitt and Young, 1982) (Fig. 5) defined by previous studies (Qiu et al., 2009, 2011). These observations suggest that the protoliths of the kinzigites, and not metamorphic dehydration reactions (i.e., muscovite breakdown), exerted the greatest control on their [Li].

Enrichments of Li in the pelitic sediments are linked to the abundance of Mg-bearing clay minerals, such as smectites, which play an important role in the Li geochemical cycle (Stoffyn-Egli and Mackenzie, 1984). Because of its similar ionic radius, Li$^+$ substitutes for Mg^{2+} in the octahedral sites of the clay's crystal lattice, with additional Li$^+$ going into the interlayer position for charge compensation (Williams and Hervig, 2005; Vigier et al., 2008). Fig. 6 illustrates the possible Li-

Fig. 4. Plot of Li concentrations versus biotite mode for the metapelites from the three zones. Error bars indicate 2σ uncertain of Li concentrations (± 10%).The gray trend line shows the positive correlation between [Li] and biotite modal compositions in the metapelites, except for sample P1.
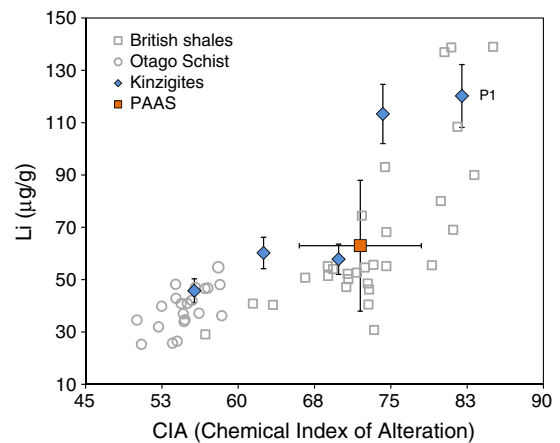

Fig. 5. Plot of Li concentrations versus CIA (Chemical Index of Alteration) for the metapelites from the kinzigite zone. PAAS: Post Archean Australian Shales. Average [Li] and CIA value of PAAS is from Teng et al. (2004).
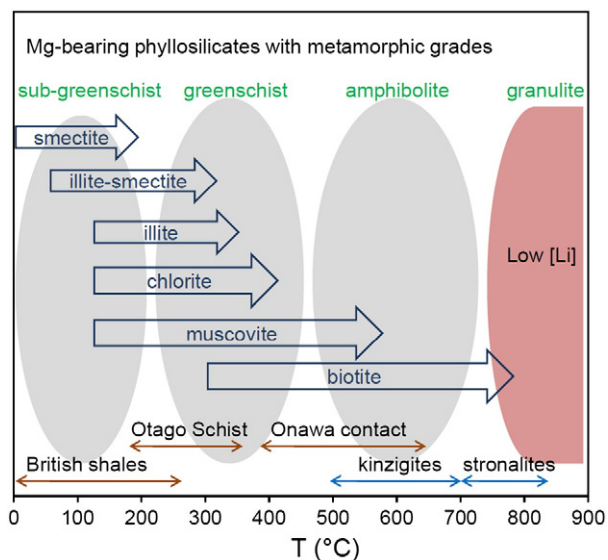
Fig. 6. Evolution of Mg-bearing phyllosilicates as a function of metamorphic grade in pelitic sediments. The ellipses indicate the sequence of metamorphism from sub-greenschist to granulite facies. The Mg-bearing phyllosilicates listed on the figure may contain most of Li in the metapelites. During granulite facies metamorphism, most of the phyllosilicates break down, resulting in low [Li] in the rocks. The relationship between minerals and temperature is according to Eberl (1984) and Winter (2010). The temperature range of British shales, Otago Schist and Onawa contact aureole are from Qiu et al. (2009), Qiu et al. (2011) and Teng et al. (2007), respectively. See text for details.

enriched phyllosilicates present during prograde metamorphism of pelitic sediments (based on Eberl, 1984). During sedimentation and low-grade metamorphism (up to greenschist facies), the original smectite is gradually converted into mixed-layer illite–smectite and chlorite, which retain Li, since smectite, illite and chlorite are all Mg-bearing. Illitization and chloritization are the likely reasons for the lack of Li depletion during sub-greenschist facies metamorphic dehydration observed in the British shales (Qiu et al., 2009). During higher grade metamorphism (up to amphibolite facies) chlorite breaks down, but Li released from chlorites may be completely incorporated into newly formed biotite (chlorite + K-feldspar → biotite + muscovite; Spear and Cheney, 1989), and, thus, the rocks maintain the original Li signature of the protolith, as seen in the kinzigite samples. However,
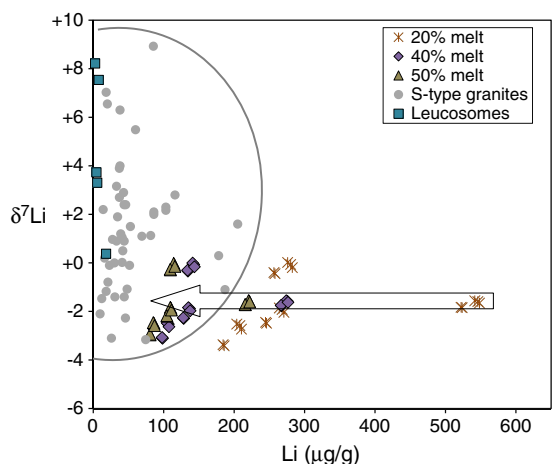

Fig. 7. Plot of [Li] and δ^7Li of calculated partial melts. Data for S-type granites (gray field) are from Teng et al. (2006b), Bryant et al. (2004) and Magna et al. (2010). The fraction of the melt in the model is 20%, 40% and 50% (see text for details). The arrow indicates compositional variation of melts produced by increasing the melt proportion.

if the metamorphic reaction causes the breakdown of Mg-bearing phyllosilicates without forming new ones, then the Li will be lost during dehydration, as observed in the granulite facies stronalites, as well as the greenschist facies Otago schist, New Zealand (Qiu et al., 2011) and amphibolite facies Onawa contact aureole, Maine, USA (Teng et al., 2007). Thus, a key factor determining the [Li] of metapelites during metamorphism might be the stability of Mg-bearing phyllosilicates.

5.2. Factors controlling the δ^7Li of metapelites

In contrast to [Li], no significant difference is observed in the average δ^7Li values of kinzigites, transition, and stronalite zone rocks (Fig. 2), demonstrating that metamorphic dehydration in stronalites has no appreciable effect on the whole rock δ^7Li, and the δ^7Li values of the metapelites likely reflect the signature of their protoliths.

One unusual kinzigite sample (P1) has the lowest δ^7Li (−8.4), most abundant [Li] (120 µg/g) (Fig. 2) and highest CIA (82) value of the suite (Fig. 5). The highly weathered protolith signature of this sample is also reflected in its markedly low concentrations of Sr and Ba (Table 2), which are characteristics of chemical weathering of feldspar resulting in loss of these soluble elements. Therefore, the Li composition of sample P1 may reflect the influence of severe weathering in the provenance of the sediment, which concentrates ^6Li relative to ^7Li in the regolith (Kisakurek et al., 2004; Rudnick et al., 2004; Qiu et al., 2009). Moreover, the abnormally low δ^7Li of P1 may also reflect Li addition through diffusion. Since ^6Li diffuses faster than ^7Li, significant isotopic fractionation occurs during diffusion (e.g., Richter et al., 2003; Lundstrom et al., 2005; Teng et al., 2006a; Jeffcoate et al., 2007; Penniston-Dorland et al., 2010; Halama et al., 2011; Verney-Carron et al., 2011). Therefore, if Li diffused into this sample, it would create low δ^7Li and elevated [Li]; the field evidence that sample P1 includes numerous quartz veins may reflect the infiltration of hydrothermal fluids, though based on the study of the Otago Schists (Qiu et al., 2011), one would predict that hydrothermal fluids may have little leverage on Li in such a Li-rich lithology. The fact that this sample plots above the trend in the modal biotite vs. [Li] plot (Fig. 4) and below the trend in the [Li] vs. δ^7Li plot (Fig. 2) supports the possibility of Li diffusion. Thus, either of these two processes (weathering and diffusion), or both, may have played a role in producing the distinctive composition of this sample, and a study at the outcrop scale of this locality is needed to provide further information necessary to resolve this issue.

The reason for the lack of significant Li isotopic fractionation during metamorphism is apparent from studies of Li isotopic fractionation factors, α or $\Delta_{fluid-rock}$. Most such factors are inferred from the interaction between seawater and basalts (Chan and Edmond, 1988; Chan et al., 1994; James et al., 1999; Millot et al., 2010) or determined from equilibration experiments between fluids and minerals (Wunder et al., 2006, 2007; Vigier et al., 2008). The isotopic fractionation factors inferred from these studies give $\Delta_{solution-rock(mineral)}$ values of 1 to 3‰ at 500–900 °C, 1 to 5‰ at 250 °C, ~10‰ at 150 °C and ~19‰ at 2 °C. These experimental results show that equilibrium isotopic fractionation of Li is limited or analytically unresolvable at temperatures above 250 °C, which is generally the temperature for sub-greenschist facies metamorphism. Consequently, Li loss during higher-grade metamorphism may not result in discernable Li isotopic fractionation.

5.3. Li signature of leucosomes

The average [Li] of the leucosomes is significantly lower than that of the metapelites from the same metamorphic zone (Fig. 3), consistent with the mineralogy of the leucosomes (mainly quartz and minor feldspar, which typically have low Li concentrations), which lack a Li-rich phase such as biotite. Leucosomes from the stronalite zone, interpreted as partial melt products (Bea and Montero, 1999), have, on average, higher δ^7Li than those of the metapelites from the same zones

(Fig. 3). This difference may reflect equilibrium Li isotopic fractionation accompanying crystallization of the leucosomes from a melt having an isotopic composition similar to the stronalites, as quartz preferentially takes ^{7}Li into its two- and four-fold-coordinated interstitial sites during crystallization (Sartbaeva et al., 2004; Teng et al., 2006b). However, due to the lack of any Li partitioning data between quartz and melt, it is unknown whether significant isotopic fractionation can be generated at the implied temperatures of vein formation (~800 °C) (Bea and Montero, 1999).

Leucosomes in the kinzigite zone, interpreted to have precipitated from hydrothermal fluids (Bea and Montero, 1999), are more quartz- and Na-rich and K-poor when compared to those in the stronalite zone. Since quartz preferentially takes ^{7}Li from fluids into its structure and hydrothermal fluids generally have relatively heavy Li isotopic compositions ($+4$ to $+30$, Foustoukos et al., 2004; Millot et al., 2010 and references therein), these leucosomes from the kinzigite zone should have lower [Li] and higher δ^7Li relative to the leucosomes from the stronalite zone. However, the opposite is true. Qiu et al. (2011) reported surprisingly light Li isotopic composition for fluid-precipitated quartz veins in the Otago Schists, which have δ^7Li similar to that of their enclosing wall rocks (δ^7Li = -1.4 to -2.8). These isotopic values were interpreted to reflect the influence of Li ingress from surrounding wallrock, i.e., ^{6}Li diffuses more rapidly than ^{7}Li from wallrocks into leucosomes in the kinzigite zone. A similar explanation may hold for the fluid-precipitated leucosomes in the kinzingite zone. The somewhat higher [Li] in these leucosomes (12–15 µg/g) compared to that of the quartz veins in the Otago Schists ([Li] = 0.4 to 2.3 µg/g, Qiu et al., 2011) may reflect the generally higher [Li] in the Ivrea kinzigites compared to the Otago Schists (Fig. 2) and the presence of feldspar and garnet, in addition to quartz in the Ivrea leucosomes.

5.4. Li depletion and partial melting

The significant depletion of Li in the metapelites, which appears to accompany granulite-facies partial melting/dehydration is not accounted for by Li contained within the leucosomes from the stronalite zone. Large amounts of Li must have been removed from the system. One possible scenario is the extraction of a granitic melt that ascended into the upper crust, leaving a refractory granulite restite depleted in incompatible elements (Schnetger, 1994; Quick et al., 2009).

In order to model the change in [Li] during partial melting, we apply a batch melting model that uses the composition of the kinzigites and stronalites to represent the composition of the parent rocks and the restites, respectively. The partial melting model of Schnetger (1994) suggested that granulite facies partial melting produced about 40% melt with a composition similar to average S-type granite. However, [Li] in the model melt (>100 µg/g) is higher than [Li] in average S-type granite (<100 µg/g). Schnetger (1994) suggested that this discrepancy may be due to insufficient Li data for S-type granites or that Li is lost from the granite during pegmatite formation. More recent [Li] and δ^7Li data for S-type granites (Bryant et al., 2004; Teng et al., 2006b; Magna et al., 2010) provide a further opportunity to evaluate these possibilities.

Following Schnetger (1994), we apply a batch melting model, $C_i = [C_0 - (1 - F) C_s]/F$, in which C_i is the calculated composition of the granitic melt, C_0 is the composition of the parent rocks (kinzigites), F is the melt fraction and C_s is the composition of the restite (stronalites). In order to investigate the possible range of melt compositions, each kinzigite and stronalite sample measured in this study (excluding P1) is considered as the individual composition of parent rock and restite, respectively, and the volume of melt is allowed to vary between 20 and 50% (possible melt volume generated from partial melting of kinzigites; Schnetger, 1994). Fig. 7 shows the modeling results for [Li] and δ^7Li in the granitic melt, which is compared with data for S-type granites. Model C_i compositions that plot within the range of S-type granites (gray field, Fig. 7) are derived from 40 to 50% partial melting of kinzigites having low [Li] (in the range of 46 to 60 µg/g); this partial melting process results in a

bulk $^{solid/melt}D_{Li}$ of 0.05 to 0.14, which reflects the highly incompatible behavior of Li. Partial melting of parent rocks with high [Li] (60–113 µg/g) produces melts having higher [Li] than any S-type granite analyzed, to date. For this subset of Li-enriched melts, additional processes must be operative.

Pegmatites are generally much more enriched in Li than S-type granites (Cerny et al., 1985; Teng et al., 2006b; Liu et al., 2010); therefore, the Li-enriched melts in the partial melting model may contribute to the formation of pegmatites. The δ^7Li of minerals from pegmatites (e.g., quartz, plagioclase, mica, spodumene, tourmaline) varies widely, but is generally heavier ($+1.5$ to $+21$, Teng et al., 2006b; Maloney et al., 2008; Liu et al., 2010) than that of the melt calculated in this study (δ^7Li of -0.3 to -3.1). Consequently, if the modeled melts contribute to the formation of pegmatites, isotopic fractionation must occur during pegmatite formation, probably during their late-stage crystallization (Teng et al., 2006b).

5.5. Li concentration and isotopic composition of lower continental crust

The stronalites, along with other granulite facies mafic–ultramafic rocks in the Ivrea–Verbano Zone, are considered as a representative section of lower continental crust (e.g., Berckhem, 1969; Fountain, 1976; Voshage et al., 1990). Moreover, the average composition of the stronalties in this study is similar to the average composition of lower continental crust in terms of SiO_2 and $Na_2O + K_2O$ (e.g., 52.1% and 3.0%, respectively, for the stronalites, cf. 53.4% and 3.26%, respectively, for the estimated lower crust of Rudnick and Gao, 2003). Therefore, the Li composition of the stronalites may provide insight into the Li signature of the lower continental crust.

The stronalites have [Li] of 5–11 µg/g (average 8 ± 6 µg/g, 2σ) and δ^7Li of -1.1 to $+2.1$, (average = 0.9 ± 2.9, 2σ), with a concentration weighted average δ^7Li of $+1.1$. This [Li] is comparable to that previously estimated for the lower crust (between 6 and 14 µg/g, Taylor and McLennan, 1985; Shaw et al., 1994; Wedepohl, 1995; Rudnick and Fountain, 1995; Rudnick and Gao, 2003; Teng et al., 2008), and is identical to the value determined by Teng et al. (2008) for the lower crust based on several xenolith suites as well as granulite terrane composites.

The low and near constant δ^7Li values of stronalites stand in contrast to the results of Teng et al. (2008) for lower crustal xenoliths. Teng et al. (2008) suggested that the variable δ^7Li seen in the xenoliths is the result of a combination of effects, including isotopic fractionation during prograde metamorphism, kinetic fractionation caused by basaltic intrusions and variable protolith compositions. Our results suggest that prograde metamorphism (up to granulite facies) is unlikely to cause Li isotopic fractionation. Furthermore, the three granulite facies metabasites derived from the mafic protoliths have lower [Li] (average 3.6 ± 1.2 µg/g, 2σ) but average δ^7Li (-3.2 to $+3.3$, average 0 ± 6.5, 2σ), comparable to that of the stronalites derived from the felsic protoliths, indicating that heterogeneous protoliths may contribute little to the highly variable δ^7Li seen in the xenoliths by Teng et al. (2008). Therefore, kinetic isotopic fractionation is the most likely cause of the strongly heterogeneous δ^7Li in the xenoliths. It is noteworthy that one granulite metabasite (B5) has negative δ^7Li (δ^7Li = -3.2). Such low values have not been found in any mantle-derived melts and the depleted mantle is suggested to have δ^7Li of $+3.4 \pm 1.4$ (2σ) (Tomascak et al., 2008, and references therein); therefore, the low δ^7Li in this sample may have been formed kinetically.

Based upon the Li signature in stronalites and metabasites, the [Li] of lower continental crust, as sampled in the Ivrea–Verbano Zone, is around 8 µg/g or less, and the concentration weighted δ^7Li is $+1.0$.

6. Conclusions

[Li] and δ^7Li in amphibolite facies kinzigites likely reflect the Li signature of their protolith, which, in turn, reflects the composition of

the provenance of the sediments; [Li] in the metapelites positively correlates with the abundance of biotite, reflecting the influence of Mg-bearing phyllosilicates on [Li] in these rocks. Pre-granulite facies metamorphic dehydration reactions may have had minor influence on Li in the kinzigite samples; however, dehydration melting associated with biotite breakdown during granulite facies metamorphism caused extreme [Li] depletion in stronalites. The δ^7Li in both amphibolite- and granulite-facies metapelites is statistically indistinguishable, indicating no significant Li isotopic fractionation at these metamorphic temperatures (500–800 °C). Leucosomes in the kinzigite zone were precipitated from hydrothermal fluids, but those in the stronalite zone formed by partial melting. The low [Li] and relatively high δ^7Li of leucosomes in the stronalite zone are consistent with their origin as quartz-rich precipitates from a partial melt, since the crystallization of quartz from melts may cause significant Li isotopic fractionation. The lower δ^7Li of leucosomes in the kinzigite zone may reflect Li diffusion into the quartz-rich veins from surrounding Li-rich metapelite. A batch melting model indicates some of the Li released during partial melting of metapelites can contribute to S-type granites, with excess Li being partitioned into Li-pegmatites. The Li compositions in stronalites and metabsites indicate that the lower continental crust, as represented by the Ivrea–Verbano Zone, has [Li] of 8 μg/g or less, and a concentration weighted δ^7Li of + 1.0.

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