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., Marshall et al., 2007; Teng et al., 2007) in order to understand the distribution of Li concentrations ([Li]) and isotopic compositions ([27Li/26Li]) of amphibolite- to granulite-facies metapelites, leucosomes and metabasites from the Ivrea–Verbano Zone, NW Italy. The average [Li] of amphibolite-facies kinzigites (79±6 μg/g, 2σ) is higher than that of granulite-facies stronalites (8±6 μg/g, 2σ) that experienced partial melting via biotite dehydration reactions. Biotite breakdown, there is no significant change in [27Li], which averages 1.4±2.0 (2σ, excluding an anomalously light sample) in the kinzigites (amphibolite facies) and +0.9±2.9 (2σ) in the stronalites (granulite facies). Both average [27Li] values are comparable with those of other pelitic sediments and likely reflect the [27Li] of their protoliths. An anomalous kinzigitic sample, with the lowest [27Li] (−8–4) and the highest [Li] (120 μg/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 [27Li]. 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±2.6 μg/g (2σ) and are isotopically similar to the kinzigites ([27Li]=−1.0±0.2, 2σ) while the latter formed by dehydration melting and have lower [Li] (3±2.6 μg/g, 2σ) that is heavier ([27Li]=+6.0±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 [27Li] of −3.2 to +3.3 (average 0±6.3, 2σ). While these concentrations are typical of those of possible basaltic protoliths, the highly variable [27Li] suggests Li mobility during metamorphism. Collectively, the Li signatures in granulate-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 [27Li] of this section of the lower continental crust is +1.0, which is similar to a previous estimate (8 μg/g, +2.5).

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 ([27Li/26Li]) 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±6 μg/g, 2σ) is higher than that of granulite facies stronalites (8±6 μg/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 [27Li], which averages 1.4±2.0 (2σ, excluding an anomalously light sample) in the kinzigites (amphibolite facies) and +0.9±2.9 (2σ) in the stronalites (granulite facies). Both average [27Li] values are comparable with those of other pelitic sediments and likely reflect the [27Li] of their protoliths. An anomalous kinzigitic sample, with the lowest [27Li] (−8–4) and the highest [Li] (120 μg/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 [27Li]. 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±2.6 μg/g (2σ) and are isotopically similar to the kinzigites ([27Li]=−1.0±0.2, 2σ) while the latter formed by dehydration melting and have lower [Li] (3±2.6 μg/g, 2σ) that is heavier ([27Li]=+6.0±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 [27Li] of −3.2 to +3.3 (average 0±6.3, 2σ). While these concentrations are typical of those of possible basaltic protoliths, the highly variable [27Li] suggests Li mobility during metamorphism. Collectively, the Li signatures in granulate-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 [27Li] of this section of the lower continental crust is +1.0, which is similar to a previous estimate (8 μg/g, +2.5).
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). 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 granulate-facies xenoliths from China and Australia, Teng et al. (2008) found the lower crust to be strongly heterogeneous in δ7Li, with δ7Li 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 δ7Li 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, magmatized metapelites and metapsammite (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
biotite is completely replaced by garnet in granulite-facies metapelites, which are locally called stronalites (Bertolani and Garuti, 1970; Luvisotto and Zacc, 2009). In this study, 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 metapelites, 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 metapelites 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 previously been analyzed for major and trace elements by 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 metapelites were collected from the stronalite zone; their compositions are reported in Tables 3 and 2, respectively.

4. Results

Lithium concentrations and isotopic compositions of the metapelites, leucosomes and metapelites 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–HNO3–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 micro-nebulizer 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/min. The Li and Li 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 1011 Ω 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 [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 6Li of BCR-1 to be +2.0±0.7 (10 runs), 7Li = +2.7±1 (3 runs) and 7Li = +2.4±0.4 (4 runs), respectively, and the GEOREM (Jochum and Nohl, 2008) preferred BCR-1 [Li] = 13±1 µg/g.

Lithium concentrations and isotopic compositions of the metapelites, leucosomes 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-SCLIF-ELAN5000 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

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**Table 1**

<table>
<thead>
<tr>
<th>Kinzigites</th>
<th>Transition</th>
<th>Stronalites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample no.</td>
<td>P1</td>
<td>P2</td>
</tr>
<tr>
<td>Estimated PT conditions</td>
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<td></td>
</tr>
<tr>
<td>P&lt;sub&gt;0.9mm&lt;/sub&gt; (GPa)</td>
<td>0.40</td>
<td>0.42</td>
</tr>
<tr>
<td>T&lt;sub&gt;b&lt;/sub&gt; (°C)</td>
<td>500</td>
<td>560</td>
</tr>
<tr>
<td>Modal composition (wt.%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orthopyroxene</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Cordierite</td>
<td>2.6</td>
<td>n/a</td>
</tr>
<tr>
<td>Biotite</td>
<td>25.6</td>
<td>21.9</td>
</tr>
<tr>
<td>Garnet</td>
<td>0.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Sillimanite</td>
<td>10.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Quartz</td>
<td>49.5</td>
<td>51.6</td>
</tr>
<tr>
<td>K-feldspar</td>
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<td>2.7</td>
</tr>
<tr>
<td>Plagioclase</td>
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<td>17.3</td>
</tr>
<tr>
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<td>0.37</td>
</tr>
<tr>
<td>Monazite</td>
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<td>0.024</td>
</tr>
<tr>
<td>Xenotime</td>
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<td>0.001</td>
</tr>
<tr>
<td>Zircon</td>
<td>0.051</td>
<td>0.022</td>
</tr>
<tr>
<td>Others*</td>
<td>0.80</td>
<td>0.85</td>
</tr>
</tbody>
</table>

* ilmenite + rutile + graphite + sulfides.

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Author's personal copy
trace elements are from Bea and Montero (1999).

The uncertainties for $[\text{Li}]$ (mg/g) differ by about two orders of magnitude (a few
than one order of magnitude) will not influence the discussion and conclusions related to the metamorphic effects. Additionally, the average uncertainties; $\sigma_{\text{fl}}$ fluence on the estimates of $[\text{Li}]$ between low- and high-grade metapelites vary widely (Tables 2 and 4), 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 $[\text{Li}]$ for kinzigite zone generally 10–50% higher than the value determined in this study. However, since the $[\text{Li}]$ 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 $[\text{Li}]$ 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 $[\text{Li}]$ of granulite-facies samples (stronalites and metabasites) differ between the two studies generally overlap, considering the 2σ uncertainties; therefore, the discrepancy has only a minor influence on the estimates of $[\text{Li}]$ in the lower continental crust. We also report both the arithmetic and log-normal mean of $[\text{Li}]$ 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).
The uncertainties of the average Li determined in our study. The Li of three samples are 15 μg/g from Bea and Montero (1999).

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).

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Kinzigites</th>
<th>Transition</th>
<th>Stronalites</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>1.0</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>L2</td>
<td>1.4</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>L3</td>
<td>1.6</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>L4</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>L5</td>
<td>1.6</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>L7</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>L8</td>
<td>1.6</td>
<td>1.4</td>
<td>1.5</td>
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<table>
<thead>
<tr>
<th>δ7Li</th>
<th>a (μg/g)</th>
<th>b (μg/g)</th>
<th>c (μg/g)</th>
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</thead>
<tbody>
<tr>
<td>Mean</td>
<td>103</td>
<td>41</td>
<td>8</td>
</tr>
</tbody>
</table>

**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).**

<table>
<thead>
<tr>
<th>From</th>
<th>Kinzigites</th>
<th>Transition</th>
<th>Stronalites</th>
<th>Leucosomes</th>
<th>Metabasites</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.</td>
<td>5</td>
<td>14</td>
<td>38</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Max.</td>
<td>120</td>
<td>81 n/a</td>
<td>42</td>
<td>11</td>
<td>70 n/a</td>
</tr>
<tr>
<td>Min.</td>
<td>46</td>
<td>16 n/a</td>
<td>39</td>
<td>5</td>
<td>2 n/a</td>
</tr>
<tr>
<td>Mean</td>
<td>79</td>
<td>57 103</td>
<td>41</td>
<td>8</td>
<td>14 15</td>
</tr>
<tr>
<td>Mean (LN)</td>
<td>74</td>
<td>41</td>
<td>6</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

**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 (lock/fluid D_li) that negatively correlates with

Li concentrations 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 2σ 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 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 δ7Li of one anomalously light sample (P1, δ7Li = −8.5) is not included in the average δ7Li of kinzigites, since it is a statistical outlier (plotting outside of the "outer fence", defined by 3σ interquartile range). This sample’s unusual composition is discussed in Section 5.2. The average δ7Li of kinzigites, δ7Li = −1.4 ± 2.0 (2σ), is indistinguishable from that of the transition (δ7Li = +0.4) and stronalite (average = +0.9 ± 2.9, 2σ) zones. The δ7Li values of the leucosomes get progressively heavier from the kinzigite (−0.9 to −1.1, average δ7Li = −1.0 ± 0.2, 2σ) to transition (+3.3 to +7.5, average δ7Li = +5.4 ± 6.0, 2σ) to stronalite (δ7Li = +6.0 ± 3.2, 1σ) zones (Fig. 3b). The granulite metabasites have δ7Li of −3.2 to +3.3 (average 0.6 ± 3.2, 2σ), which overlap those of the stronalites.

Fig. 2. Plot of δ7Li versus [Li] for metapelites from the three zones. Error bars indicate the 2σ uncertainty of Li isotopic compositions (±1σ) 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.
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):

\[
\text{biotite} + \text{sillimanite} + \text{plagioclase} + \text{quartz} \rightarrow K\text{-feldspar} + \text{garnet} + \text{rutile} + \text{melt}
\]

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):

\[
\text{muscovite} + \text{quartz} \rightarrow \text{sillimanite} + K\text{-feldspar} + H_2O
\]
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 diageneic 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 (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 Mg²⁺ 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. 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 greenschist 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 contain 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, 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 stromatolites, 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 \( \delta^7\text{Li} \) of metapelites

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

One unusual kinzigite sample (P1) has the lowest \( \delta^7\text{Li} \) (−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 Li relative to \( ^7\text{Li} \) in the regolith (Kisakurek et al., 2004; Rudnick et al., 2004; Qiu et al., 2009). Moreover, the abnormally low \( \delta^7\text{Li} \) of P1 may also reflect Li addition through diffusion. Since \( ^7\text{Li} \) diffuses faster than \( ^6\text{Li} \), 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 \( \delta^7\text{Li} \) 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. \( \delta^7\text{Li} \) 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, or \( \Delta_{\text{fluid-rock}} \). Most such factors are inferred from the interaction between seawater and basalts (Chan and Edmond, 1988; Chan et al., 1994; James et al., 1999; Millet 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 \( \Delta_{\text{fluid-rock}} \) 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 stromatolite zone, interpreted as partial melt products (Bea and Montero, 1999), have, on average, higher \( \delta^7\text{Li} \) than those of the metapelites from the same zones.
addition to quartz in the Ivrea leucosomes. The Otago Schists (Fig. 2) and the presence of feldspar and garnet, in may re
quartz veins in the Otago Schists ([Li] = 0.4 to 2.3
Since quartz preferentially takes $^7\text{Li}$ from
and Na-rich and K-poor when compared to those in 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 $^{6}\text{Li}$ similar to that of their enclosing wall rocks ($^{6}\text{Li} = 1.4$ to $2.8$). These isotopic values were interpreted to reflect the influence of Li ingress from surrounding wallrock, i.e. Li diffuses more rapidly than $^7\text{Li}$ from wallrocks into
to its two- and four-fold-coordinated
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 $^7\text{Li}$ 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 $^{6}\text{Li}$ relative to the leucosomes from
the stronalite zone. However, the opposite is true. Qiu et al. (2011)
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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
stronger Li isotopic composition in the Otago Schists (~800 °C) (Bea and Montero, 1999).
Following Schnetger (1994), we apply a batch melting model, $C_i = \left[C_i - \left(1 - F\right) C_j/F\right]$, in which $C_i$ is the calculated composition of the granitic melt, $C_j$ is the composition of the parent rocks (kinzigites), $F$ is the melt fraction and $C_i$ 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 $^{6}\text{Li}$ 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 (grey 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 $D_{\text{Li}}$ 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 $^{6}\text{Li}$ 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 ($^{6}\text{Li}$ 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 stratolites, 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 stratolites in this study is similar to the average composition of lower continental crust in terms of SiO$_2$ and Na$_2$O+K$_2$O (e.g., 52.1% and 3.0%, respectively, for the stratolites, cf. 53.4% and 3.26%, respectively, for the estimated lower crust of Rudnick and Gao, 2003). Therefore, the Li composition of the stratolites may provide insight into the Li signature of the lower continental crust.
The stratolites have [Li] of 5–11 μg/g (average 8 ± 6 μg/g, 2σ) and $^{6}\text{Li}$ of −1.1 to +2.1, (average 0.9 ± 2.9, 2σ), with a concentration weighted average $^{6}\text{Li}$ 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; Weperski, 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 $^{6}\text{Li}$ values of stratolites stand in contrast to the results of Teng et al. (2008) for lower crustal xenoliths. Teng et al. (2008) suggested that the variable $^{6}\text{Li}$ 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 metabasalts derived from the mafic protoliths have lower [Li] (average 3.6 ± 1.2 μg/g, 2σ) but average $^{6}\text{Li}$ of −3.2 to +3.3, average 0 ± 6.5, 2σ, comparable to that of the stratolites derived from the felsic protoliths, indicating that heterogeneous protoliths may contribute little to the highly variable $^{6}\text{Li}$ seen in the xenoliths by Teng et al. (2008). Therefore, kinetic isotopic fractionation is the most likely cause of the strongly heterogeneous $^{6}\text{Li}$ in the xenoliths. It is noteworthy that one granulite metabasite (B5) has negative $^{6}\text{Li}$ ($^{6}\text{Li} = 32.9$). Low values have not been found in any mantle-derived melts and the depleted mantle is suggested to have $^{6}\text{Li}$ of +3.4 ± 1.4 (2σ) (Tomascak et al., 2008, and references therein); therefore, the low $^{6}\text{Li}$ in this sample may have been formed kinetically.
Based upon the Li signature in stratolites and metabasalts, the [Li] of lower continental crust, as sampled in the Ivrea–Verbano Zone, is around 8 μg/g or less, and the concentration weighted $^{6}\text{Li}$ is +1.0.
6. Conclusions
$^{6}\text{Li}$ and $^{6}\text{Li}$ in amphibolite facies kinzigites likely reflect the Li signature of their protolith, which, in turn, reflects the composition of
compositions in stronalites and metapsites indicate that the lower
metapelite. A batch melting model indicates some of the Li released
re
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phic 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 δ7Li 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 δ7Li of leucosomes in the kinzigite zone may reflect Li diffusion into the quartz-rich veins from surrounding Li-rich metapelites. 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 metabasites 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 δ7Li of +1.0.

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