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A lithium isotopic study of sub-greenschist to greenschist facies metamorphism in an accretionary prism, New Zealand

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ABSTRACT

To investigate the behavior of Li during low-grade metamorphism and fluid flux in an accretionary prism we measured the Li concentrations ([Li]) and isotopic compositions (δ^7Li) of sub-greenschist and greenschist-facies Otago Schist composites, as well as cross-cutting quartz veins, which are interpreted to have precipitated from slab-derived fluids. The average [Li] of sub-greenschist facies composites (41 ± 13 μg/g, 2σ) is statistically distinct (97% confidence level, student t test) to that of greenschist facies composites (34 ± 9 μg/g, 2σ), which have experienced mass addition of silica in the form of quartz veins having [Li] between 0.4–2.3 μg/g. A linear regression of the correlation between [Li] and calculated mass additions suggests that the depletion of [Li] in greenschist facies composites is due to both dilution from the addition of the quartz veins, as well as metamorphic dehydration. The [Li] of both groups of composites correlates with their CIA (Chemical Index of Alteration) values (50–58), which are low, consistent with the inferred graywacke protolith of the Otago Schist. The δ^7Li of sub-greenschist and greenschist facies composites are remarkably constant, with an average δ^7Li of 0.2 ± 1.7 (2σ) and -0.5 ± 1.9 (2σ), respectively, and comparable to that of the average upper continental crust. Thus, metamorphism has had no discernable effect on δ^7Li in these samples. The Li isotopic signature of the schists is similar to that seen in pelitic sedimentary rocks and likely reflects the δ^7Li of the protoliths. The surprisingly light δ^7Li of the quartz veins (−2.8 to −1.4) likely records kinetic fractionation associated with Li ingress into the veins from surrounding wallrock.

An isotopic equilibrium fluid flow model indicates that: 1) if the [Li] of slab-derived fluids is less than a few μg/g, the δ^7Li of the overlying lithologies (i.e., the schists) is not significantly influenced by the fluid flux, regardless of the δ^7Li of the fluids, 2) the slab-derived fluids will have heavy δ^7Li of $> +10$ after reacting with the prism sediments during their ascent, and 3) the [Li] of the slab-derived fluids is likely in the range of $0 < [Li] \leq 41$ (μg/g). Thus, isotopically heavy slab-derived fluids that traverse sediments in accretionary prisms may leave little trace in the rocks and their surface compositional characteristics will reflect the net result of their interaction with the sediments of the prism.

1. Introduction

The fluid-mobile element lithium increasingly receives attention because of the large isotopic fractionation in δ^7Li that can occur at the Earth's surface and its possible usefulness as a tracer of crustal recycling in subduction zones (e.g., Elliott et al., 2004, 2006 and references therein). Nevertheless, Li isotopic fractionation during low-grade metamorphism, particularly during subduction-zone metamorphism, remains a matter of debate (e.g., Marschall et al., 2007; Zack et al., 2003).

Recent findings reveal that metamorphic dehydration has had little discernible effect on δ^7Li, even in the presence of lithium depletion (Marschall et al., 2007; Qiu et al., 2009; Teng et al., 2007). For example, the Li isotopic compositions of mudrocks from basins in the British Caledonides are unaffected by sub-greenschist facies metamorphism and reflect the Li isotopic signature of the protoliths (Qiu et al., 2009). However, metamorphism in the British mudrocks occurred at shallow depths, where initial dewatering occurs and pore water in the sediments dominates the fluid flux. Fluid flux and metamorphism occurring at deeper levels within accretionary prisms may be more complex. For example, greenschist facies metamorphism in an accretionary prism can be accompanied by ingress of large volumes of fluids derived from metamorphic dehydration of the subducting slab. These fluids may interact with the overlying metamorphic rocks to form quartz veins (Breeding and Ague, 2002; Kerrich, 1999, Smith and Yardley, 1999).

To date, the signature of Li in greenschist facies metamorphic rocks from accretionary prisms and associated fluid fluxing have not been investigated. Here, we report the Li concentrations and isotopic compositions of the Otago Schist, New Zealand, which constitutes a

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typical sequence of sub-greenschist to highly veined greenschist facies meta-graywackes and metapelites that formed in an accretionary prism (Bishop, 1972; Mortimer, 1993; Rahl et al., 2011). The results from this study offer insights into the behavior of Li during low-grade metamorphism, the factors controlling the Li isotopic composition of accretionary prism sedimentary rocks and, for the first time, provide information about the behavior of Li during fluid fluxing in an accretionary prism.

2. Geological background and samples

The Otago Schist is one of the three geographically discrete units of the Mesozoic Haast Schist belt, New Zealand; the other two are the Marlborough and Alpine Schists. The Otago Schist, comprising the Permian–Cretaceous Torlesse and Caples terranes (Fig. 1), forms an approximately 150-km-wide structural arch, with prehnite–pumpellyite facies on the two outer flanks and greenschist facies in the center. The protoliths of the schist, principally graywacke–mudstone turbidites, were deposited and metamorphosed during subduction (Mortimer, 2000, 2003) and the burial and exhumation processes in the accretionary prism are recorded in these regional metamorphic rocks (e.g., Batt et al., 2001).

The composite samples of the Otago Schist (Fig. 1, 17 composites from Torlesse terrane and four composites from the Caples terrane) were collected using a traverse sampling technique in order to measure bulk compositions of whole outcrops as a function of metamorphism (Breeding and Ague, 2002). In this method, representative samples (~3–16 kg) were collected at regular intervals along a measuring tape laid out at a high angle to lithologic layering or foliation. The average traverse was ~50-meters long and comprised 26 samples. After pulverizing, two grams of each of the 26 samples were

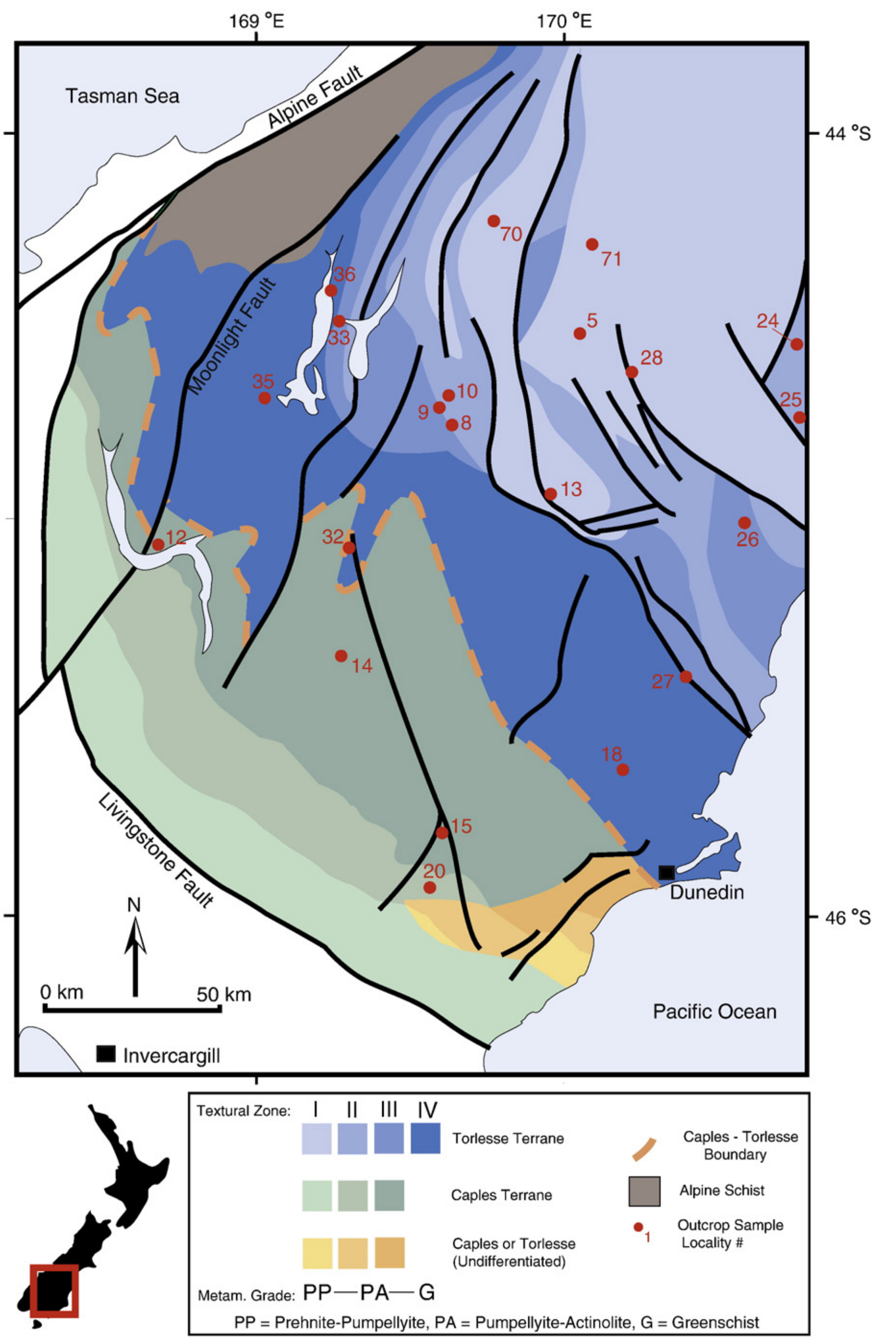

Fig. 1. Sketch map showing the sample location of Otago Schist, New Zealand (from Breeding, 2004). "Texture zones" indicate the degree of macroscopic deformation textures of the minerals, with zone I being least deformed and zone IV being most deformed (Breeding, 2004).