

# Extremely light Li in orogenic eclogites: The role of isotope fractionation during dehydration in subducted oceanic crust

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## Abstract

Eclogites from Trescolmen, Switzerland, derive from basaltic protoliths that experienced variable degrees of low-*T* seafloor alteration prior to high pressure metamorphism.  $\delta^7\text{Li}$  of the eclogites ( $-11$  to  $+5\text{‰}$ ) ranges to dramatically lower values than observed in fresh MORB, or altered MORB ( $+4.5$  to  $+14\text{‰}$  for low-*T* and  $-2$  to  $+8\text{‰}$  for high-*T* altered MORB). These low values cannot be explained by fluid interaction with surrounding garnet mica schist, which is generally isotopically heavier ( $\delta^7\text{Li}$  of  $+2.4$  to  $+3.8\text{‰}$ ). The low  $\delta^7\text{Li}$  values were likely produced by isotope fractionation through Rayleigh distillation during dehydration of clays and/or chlorite at early stages of metamorphism. These data are consistent with isotopically heavy Li being released into the forearc mantle wedge in subduction zones, while an isotopically light component is subducted deeply, and may form a distinct mantle reservoir that could be sampled by plume-related magmas.

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## 1. Introduction

Lithium is a fluid mobile alkali metal [1–3] that can be used to track fluid processes in the mantle. It is moderately incompatible during partial melt-

ing [4], and is incorporated into mantle minerals at the ppm level [5–7]. Moreover, the large mass difference ( $\sim 15\%$ ) between its two isotopes,  $^6\text{Li}$  and  $^7\text{Li}$ , produces large isotopic fractionation in terrestrial systems (from  $-10$  to  $+40\text{‰}$ ; [8]). For these reasons, Li isotopes have recently been employed to study subduction zone rocks in order to elucidate the fluid transfer processes occurring there.

Components entering subduction zones are known to have mostly heavy Li isotopic compositions compared to mid-ocean ridge basalts (MORBs) (Fig. 1) (the range in  $\delta^7\text{Li}$  for fresh N-MORB is  $+1.5$  to  $+6.5\text{‰}$  [9–11];  $\delta^7\text{Li} = 1000 \times [{}^7\text{Li}/{}^6\text{Li}_{\text{sample}}/{}^7\text{Li}/{}^6\text{Li}_{\text{standard}} - 1]$ , using the

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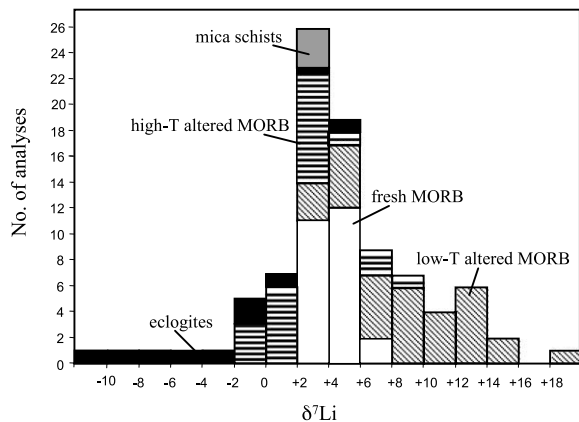


Fig. 1. Histogram of  $\delta^7\text{Li}$  analyses of fresh MORB [9–11], altered MORB [9,13], Trescolmen eclogites and garnet mica schists (this study).

National Institute of Standards and Technology standard L-SVEC; [12]). Low-temperature (<150°C) altered MORB [9,13] and pelagic sediments [14,15] are enriched in  $^7\text{Li}$  relative to fresh MORB. High-temperature (>150°C) altered MORBs range to lower values (–2.0 to +7.4‰ [13]) but are concomitantly lower in Li (mean concentration 1.0–2.5 ppm, depending on alteration style [13]) and their contribution to the subducted Li component may therefore be less significant. Thus slab-derived fluids are expected to have generally high  $\delta^7\text{Li}$  values and Li may thus be a useful tracer for the slab component in island arc volcanic rocks [10,15–18]. However, Tomascek et al. [16] caution that this simplification is valid only as long as no data exist to evaluate the degree of Li isotope fractionation during devolatilization of the subducting slab.

Isotopic fractionation during prograde metamorphism is well-established for other light elements like nitrogen [19,20] and boron [21,22], but the degree of Li isotope fractionation during dehydration reactions has yet to be determined. In this regard we measured Li isotopes in a suite of well-characterized high pressure rocks from Trescolmen (Adula nappe, Central Alps, Switzerland) that experienced extensive dehydration during high pressure metamorphism [23–25]. The strong  $^7\text{Li}$  depletions in these eclogites combined with Li data from other parts of the subduction environment shed new light on the behavior of Li iso-

topes during slab devolatilization and may ultimately improve our ability to understand the Li isotopic composition of island arc volcanic rocks and track recycled Li in the mantle.

## 2. Geology and geochemistry of high pressure rocks from Trescolmen

The area around the Lagh de Trescolmen is characterized by an abundance of fresh eclogite bodies enclosed in garnet mica schists [26–28]. A number of eclogites from Trescolmen are virtually unaffected by retrograde metamorphism during subsequent uplift, while most garnet mica schists suffered minor retrogression at amphibolite-facies conditions (e.g. growth of biotite at the expense of phengite [29]). The nappe where Trescolmen is situated (the Adula nappe) is interpreted to be the outermost passive margin of Europe that was, due to its thinness, subducted to eclogite-facies conditions during the collision with the Apulian plate in the Eocene [30]. Phase equilibrium constraints on both eclogites and garnet mica schists indicate peak pressure–temperature ( $PT$ ) conditions of around 2.4 GPa and 650°C and a major re-equilibration at slightly lower pressure (2.0 GPa) at similar temperatures [23,29,30]. Such  $PT$  conditions are also found at the top of a young subducting slab, such as that underneath SW Japan [31], and thus these eclogites provide an analog for oceanic crust subducted along a warm geotherm [24].

Compositionally, the Trescolmen eclogites are comparable to MORB in terms of major element fractionation trends and have identical concentration patterns of immobile trace elements, such as Ti, Zr and Y. However, unlike MORB, the rocks are light rare earth element (LREE)-enriched, suggesting they experienced sea-floor LREE enrichment, a possible derivation from an enriched mantle source, or interaction with continental crust. In addition, the mobile elements Na and K are enriched in some samples relative to fresh MORB glasses [23,24]. Even though the geotectonic setting for the intrusion/eruption of the Trescolmen protoliths is probably the transition between a thinned continental crust and oceanic

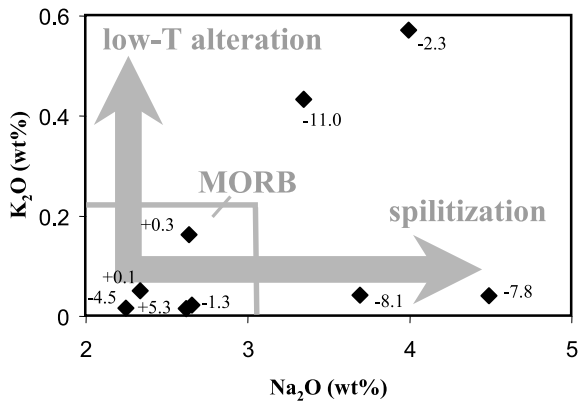


Fig. 2. Whole rock  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  composition of Trescolmen eclogites. Numbers next to data points are  $\delta^7\text{Li}$  (in ‰) of omphacite separates. Also shown is the field of fresh MORB [73] and trends of low- $T$  alteration and spilitization (see text for explanation).

crust in a passive margin setting, eruption of the Trescolmen basaltic protoliths onto the sea floor is suggested by elevated K contents, K–Rb–Cs systematics and oxygen isotope compositions (5.5 and 7.5‰ [32]). Thus, chemical processes were likely similar to those found in a mid-ocean ridge setting. In some eclogites, high Na contents are decoupled from K contents (Fig. 2) and are best explained by spilitization during (earlier) higher- $T$  hydrothermal alteration. This spilitization was also the likely cause of enrichment of other elements like LREE, Th, U, Pb and Li, as these trace elements are weakly correlated with Na and do not follow major element trends.

Assuming isochemical metamorphism of the metasediments, the Trescolmen garnet mica schists [32] derive from a clay-rich sedimentary protolith ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of  $\leq 4$  [33]). A characteristic feature of these metapelites is a high chemical index of weathering [CIW:  $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{Na}_2\text{O}+\text{CaO})\times 100$ ] [34] of 81–91, falling into the range of highly weathered residues, similar to garnet mica schists described by Mingram [33] from the Erzgebirge. Such source rocks are consistent with the paleogeographic position of the Adula nappe at the outer passive margin of Gondwana, close to a stable platform environment [35].

Mass balance shows that omphacites contain ca. 80% of the whole rock Li in the eclogites

[24]. Omphacite separates were therefore measured in order to determine the degree that the whole rock  $\delta^7\text{Li}$  was affected by retrograde metamorphism. The degree of retrogression in the garnet mica schists is significantly greater than that in the eclogites. In particular, biotite, which grew under amphibolite-facies conditions during exhumation, can contain significant amounts of Li [36]. For this reason, white micas (phengite and minor paragonite), which are the only significant primary phases for Li in high pressure assemblages of Trescolmen garnet mica schists, were measured in order to determine the Li isotopic composition of the schists at high pressure.

### 3. Analytical methods

Rock powders are from the same samples investigated in companion studies [23,24]. These powders were produced from cm-sized splits that were individually selected for their low degree of alteration. Omphacite and phengite mineral separates were hand-picked from grain size fractions of 180–300  $\mu\text{m}$ . Avoiding acid leaching, the only cleaning procedure performed was ultrasonic bathing in Milli-Q water (18 M $\Omega$  cm) for 15 min before picking. The mineral separates are estimated to be >99% pure for phengite and >99.9% pure for omphacite separates.

Acid digestion and column chemistry methods employed in this study follow the procedures described in Tomascak et al. [37], with some minor modifications outlined below. Powdered rock and mineral separates were dissolved in a 3:1 mixture of concentrated HF–HNO<sub>3</sub> using Savillex screw-top beakers on a hot plate at  $\sim 80^\circ\text{C}$  for  $\sim 24$  h. The solutions were refluxed twice in concentrated HNO<sub>3</sub>, then dried and picked up in concentrated HCl. The HCl was fumed off at  $\sim 80^\circ\text{C}$  for 1–2 days in order to convert all fluorides into chlorides, with replenishment of the HCl as needed, until clear solutions were observed. Because of the success of this method, the use of perchloric acid can be avoided for the materials investigated in this study; perchloric acid is routinely added only for organic-rich material [38]. The only detectable residue consisted of minute rutile grains,

which are considered to be Li-free (laser ablation inductively coupled plasma mass spectrometry (ICP-MS) analyses on such rutile grains revealed Li concentrations always  $< 0.1$  ppm). The samples were then dried again and picked up in 5 ml of 1 M HNO<sub>3</sub>, which was combined with 3 ml of 100% methanol just prior to column chemistry. This solution was loaded onto 12 ml of cation exchange resin (Bio-Rad AG50W- $\times 8$ ; 200–400 mesh) contained in quartz glass columns ( $\sim 9$  mm interior diameter), which had previously been equilibrated with 0.1 M HNO<sub>3</sub> in 80% methanol. Lithium cuts, changed slightly from that described in [37], were collected between 10 and 110 ml of elution.

Prior to analyses, the Na:Li ratio of each solution was measured semi-quantitatively, as ratios greater than  $\sim 5$  cause unstable instrumental fractionation, thus inhibiting accurate Li isotope determinations [37]. A small proportion ( $\sim 20\%$ ) of samples required additional purification. This was performed using 1 ml of cation exchange resin (Bio-Rad AG50W- $\times 12$ ; 200–400 mesh) in quartz glass columns and 0.5 M HCl mixed with 30% ethanol as elutant, following the procedure of Moriguti and Nakamura [39] (their column three). All samples were then dried and picked up in the requisite quantity of 2% HNO<sub>3</sub> to make  $\sim 50$  ppb solution for MC-ICP-MS analyses.

Lithium isotopic measurements were performed on a Nu Plasma MC-ICP-MS at the University of Maryland Geochemistry Laboratory by simultaneous collection of <sup>6</sup>Li<sup>+</sup> and <sup>7</sup>Li<sup>+</sup> in opposing Faraday cups (for a complete description of analytical procedure, reproducibility and values for international standards see [38]). Samples were introduced to the plasma using a desolvating nebulizer (Cetac Technologies Aridus®) employing a PFA nebulizer (Elemental Scientific). Uptake rate varied depending on the individual nebulizer employed but ranged between 30 and 60  $\mu\text{l}/\text{min}$ . Sensitivity was on the order of 1.5–2 V <sup>7</sup>Li<sup>+</sup> ( $10^{11}$   $\Omega$  resistor) for a 50 ppb solution aspirated at 35  $\mu\text{l}/\text{min}$ .

Mass analysis of each unknown was bracketed by measurement of the L-SVEC standard and  $\delta^7\text{Li}$  values were calculated directly from the comparison of the unknown to average standard anal-

ysis (as described in [37]). Several standards (the in-house Li-UMD-1 [a purified Li solution from Alfa Aesar®] and IRMM-016 [40]) are routinely run during the course of sample analyses. Reproducibility for these materials was  $\pm 1.0\%$  ( $2\sigma$ ) over the course of the analyses performed here.

Table 1

Lithium concentrations and isotopic compositions of eclogites (whole rock and omphacite separates) and phengite separates from garnet mica schist

	Weight (mg)	K <sub>2</sub> O (wt%)	Na <sub>2</sub> O (wt%)	Li (ppm)	$\delta^7\text{Li}$ (UMD)
Eclogites					
Z6-59-1	16.7	0.01	2.64	12	+3.0
omphacite	2.6				+5.3
Z6-55-4	10.8	0.05	2.34	17	-0.4
rep.	30.4				-2.2
omphacite	1.7				-0.4
Z6-50-14	26.6	0.04	4.50	21	-4.6
omphacite	3.6			40	-7.8
Z6-50-13	23.1	0.57	4.00	19	-3.1
rep.	27.6				-1.6
2nd rep.	26.2				-2.2
omphacite	4.4			25	-2.3
Z6-55-3	16.1	0.43	3.35	40	-9.7
rep.	12.3				-9.4
omphacite	4.8			88*	-11.0
CHM30	41.7	0.02	2.66	13	-0.1
rep.	20.2				+0.9
omphacite	9.3			30	-1.3
Z8-77-5	27.1	0.16	2.64	18	+4.6
rep.	19.7				+5.2
omphacite	5.0			64	+0.3
Z6-50-2	25.1	0.04	3.70	16	-9.5
rep.	30.0				-7.4
omphacite	6.5			28	-8.1
Z6-52-1	24.6	0.01	2.25	7	-2.5
omphacite	11.6			16	-4.5
Phengite from mica schist					
Z8-59-4				22*	+2.8
Z6-61-1				38*	+3.8
Z8-58-3				75*	+2.4

K<sub>2</sub>O, Na<sub>2</sub>O and Li concentrations of whole rocks and separates are from [24], except where indicated by \*, which were measured as outlined in [24]. Replicate refers to measurements performed on repeat dissolution of the whole rock powders, and are within the  $\pm 1\%$  error limit. Sample Z8-59-4 was also measured on the P-54 at the Department of Terrestrial Magnetism and yielded a  $\delta^7\text{Li}$  value of  $+1.2\%$ .  $\delta^7\text{Li}$  values on international rock standards measured during the course of this work are:  $+4.5\%$  for BHVO-2,  $+4.7\%$  for JB-2. The pure Li standard IRMM-016 yielded a  $\delta^7\text{Li}$  of  $+0.15\%$ .

Accuracy, assessed on the basis of measurement of international rock (BHVO-2 and JB-2, Table 1) and pure Li standards (IRMM-016, Table 1) is better than  $\pm 1.0\%$  ( $2\sigma$ ) [38].

#### 4. Results

There is a good correlation between the Li isotopic composition of eclogite whole rocks and corresponding omphacite mineral separates (Fig. 3); with three exceptions, both data sets agree within analytical error ( $\pm 1\%$ ). The two whole rocks having higher  $\delta^7\text{Li}$  relative to the omphacites (Z8-77-5 and Z6-50-14) are the most retrogressed of the eclogites. In addition, sample Z6-50-14 is the only eclogite measured that contains late-stage paragonite, which grew during high pressure fluid influx from the surrounding schists [23]. Only one eclogite whole rock has  $\delta^7\text{Li}$  significantly lower than the omphacite separate (Z6-59-1).

Both omphacites and whole rock eclogites exhibit a very large spread in  $\delta^7\text{Li}$ , ranging from  $-11.0$  to  $+5.3\%$  and  $-9.7$  to  $+5.2\%$ , respectively (Table 1). These values are distinctly lower than that of low- $T$  hydrothermally altered basalts, their likely protoliths (Fig. 1). In addition, most samples are significantly lighter than MORB [9–11] and even high- $T$  altered MORB [13], with a couple (Z6-50-2, Z6-55-3) having some of the lowest  $\delta^7\text{Li}$  yet measured in terrestrial samples. In contrast,  $\delta^7\text{Li}$  values for micas from Trescolmen schists exhibit a narrow range of  $\delta^7\text{Li}$  ( $+2.4$  to  $+3.7\%$ , Table 1), overlapping with values for terrigenous sediments [10,41,42].

#### 5. Discussion

In general, there is good correspondence between the  $\delta^7\text{Li}$  of the omphacite and eclogite whole rocks. Where discrepancies exist, the whole rock data are generally heavier than the omphacites. This suggests that whole rock lithium has been variably compromised by late-stage ingress of heavier Li (through retrogression and/or exchange with the surrounding schists). For this rea-

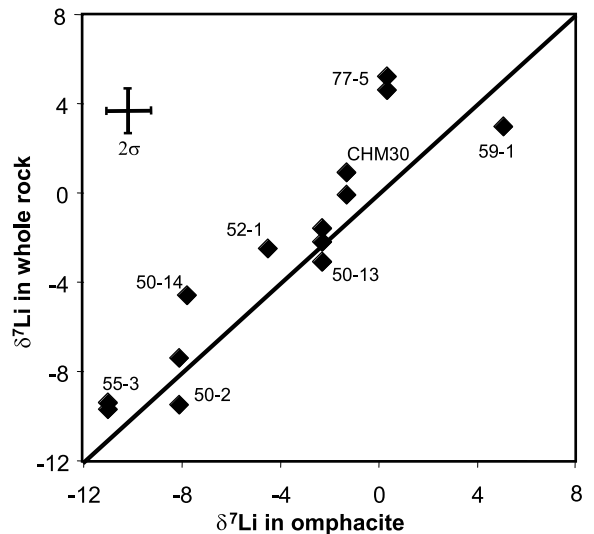


Fig. 3. Comparison between  $\delta^7\text{Li}$  of whole rock and corresponding omphacite mineral separate. Diagonal line marks a 1:1 correlation.

son the omphacite data are considered the best representative of the  $\delta^7\text{Li}$  of the dehydrated, high pressure eclogite and will be used in preference to the whole rock data in the following discussion.

##### 5.1. Processes controlling the Li budget in Trescolmen eclogites

To understand the origin of the Li isotopic variation and, in particular, the very low  $\delta^7\text{Li}$  values of some of the eclogites, one must consider the behavior of Li isotopes during all processes that potentially operated during the evolution of the Trescolmen samples. This includes seafloor alteration of the basaltic protoliths, fluid loss during prograde metamorphism, and fluid interaction between eclogite and surrounding garnet mica schist during high pressure metamorphism (by considering the omphacite values we exclude any changes in  $\delta^7\text{Li}$  due to retrograde overprinting and late-stage fluid ingress). We address each of these processes in chronological order.

##### 5.1.1. Ocean floor metamorphism

Two processes are responsible for Li enrichment in altered basalts [43]: (1) low-temperature



alteration and (2) high-temperature hydrothermal metamorphism at high water/rock ratios. Low-temperature (<150°C) alteration results in high Li concentrations due to smectite formation (up to 75 ppm [9,44]), and is generally accompanied by increased K<sub>2</sub>O ('proteceladonite' formation), high H<sub>2</sub>O contents and  $\delta^{18}\text{O}_{\text{V-SMOW}}$  (up to 3 wt%, 12 wt% and +15‰, respectively [44,45]). Similarly, high-temperature (greenschist-facies) hydrothermal metamorphism at high water/rock ratios also leads to high Li concentrations due to chlorite formation (up to 22 ppm in the oceanic crust [46] and up to 120 ppm in Variscan spilites [47]), and is accompanied by Na<sub>2</sub>O enrichment (spilitization) and heavy  $\delta^{18}\text{O}$  (up to +15‰ [47]). The  $\delta^7\text{Li}$  values in these hydrothermally altered basalts seem to be slightly elevated; two chlorite-rich samples elevated Li contents (>10 ppm) have  $\delta^7\text{Li}$  values of +5.8‰ (sample 1689-1 [9]) and +10‰ (sample 81 R 26-30 [13]).

Other types of ocean floor alteration exist, like greenschist-facies metamorphism at low fluid/rock ratios [43] and amphibolite-facies metamorphism of layers 2 and 3 of the oceanic crust. In these environments,  $\delta^7\text{Li}$  is generally light and Li abundance is depleted (−2.2 to +7.9‰ [9,13] and 0.6–4 ppm [13,43], respectively). Such rocks are mostly depleted in Na<sub>2</sub>O, K<sub>2</sub>O, and have low  $\delta^{18}\text{O}$  relative to unmetamorphosed oceanic crust [48]. However, we note that Li isotopic studies on several types of high-*T* altered basalts, e.g., amphibolite-facies overprint of layer 3 gabbros, are almost entirely absent.

The Trescolmen eclogites are characterized by high Li concentrations (Table 1), variably elevated Na<sub>2</sub>O and K<sub>2</sub>O concentrations (Fig. 2) and  $\delta^{18}\text{O}$  values higher than pristine MORB (+5.5 to +7.5‰ [32]). These features suggest that protoliths of Trescolmen eclogites were subjected to spilitization and low-*T* alteration, producing high Li concentrations and presumably high  $\delta^7\text{Li}$  values.

### 5.1.2. Fluid loss during prograde metamorphism

Trescolmen eclogites contain variable amounts of high pressure hydrous phases (e.g. phengite, amphibole, zoisite) with total whole rock H<sub>2</sub>O adding up to only ~0.5 wt%, considerably lower

than that of ordinary hydrothermally altered basalt (up to 10 wt% H<sub>2</sub>O [44]). Based on large ion lithophile element (LILE) systematics, Zack et al. [23] concluded that fluid loss during prograde metamorphism resulted in moderate depletion of very fluid-mobile elements (K, Rb, Cs) in some Trescolmen eclogites. Thus, a significant amount of water is likely to have been liberated from the Trescolmen protoliths during the course of metamorphism to the eclogite facies.

To date, Li isotopic fractionation associated with dehydration has not been demonstrated. However, the  $\delta^7\text{Li}$  values of these eclogites are lighter than any other terrestrial rock type yet measured and are thus unlikely to simply reflect protolith compositions. In addition, the known enrichment of <sup>7</sup>Li in fluids suggests that dehydration may explain the exceptionally low  $\delta^7\text{Li}$  values in these eclogite samples. We therefore explore Li isotopic fractionation by dehydration in more detail below.

### 5.1.3. Fluid exchange between metapelite and eclogite

Fluid exchange between metapelites and eclogites has been documented in Trescolmen by elevated  $\delta^{18}\text{O}$  on the rim of eclogite bodies in contact with garnet mica schist [32] and by equilibration of Cs–Rb–Ba compositions of amphibole in phengite-free eclogites with phengite of surrounding garnet mica schist [23]. Such fluid exchange could also affect the Li isotopic composition of the eclogites. The schists have generally higher Li contents and are isotopically heavier than the eclogites (i.e. +2.4 to +3.8‰ vs. −11 to +5‰). In addition, any equilibrium partitioning between fluid and schist should result in an isotopically heavy fluid. Therefore, fluid exchange is expected to make the eclogites heavier than their starting composition. Most of the eclogites have  $\delta^7\text{Li}$  below that of the schists. Thus, the unusually light lithium observed in the eclogites cannot be explained by exchange with fluids derived from the surrounding schists.

### 5.2. Li isotope fractionation during dehydration

Three factors need to be determined in order to

evaluate Li isotope fractionation during dehydration: (1) how Li isotopes fractionate as a function of temperature, (2) the fluid mobility of Li, and (3) the dehydration reactions that occurred during metamorphism.

Isotope fractionation is explained by a tendency of the lighter isotope to occupy the more highly coordinated site [49,50]. In water, the first hydration shell of Li is saturated with four H<sub>2</sub>O molecules [51], and in most silicates Li substitutes for Mg in octahedral coordination [52]. Based on these relationships, equilibrium exchange between water and Mg-silicates should lead to preferential partitioning of the heavier isotope into water, consistent with the very high  $\delta^7\text{Li}$  of seawater. In addition, studies of other stable isotope systems [53] demonstrate that mass fractionation is strongest at low temperatures. Chan et al. [9] calculated an empirical Li isotope fractionation factor ( $\alpha = ({}^7\text{Li}/{}^6\text{Li})_{\text{water}} / ({}^7\text{Li}/{}^6\text{Li})_{\text{mineral}}$ ) of 1.019 at a temperature of 2°C based on the difference of  $\delta^7\text{Li}$  between a hypothetical alteration endmember (+14‰) and seawater (+32‰). [Note that Chan et al. report  $\alpha$  in terms of  ${}^6\text{Li}/{}^7\text{Li}$  values of mineral/fluid. We report the inverse (fluid/mineral), but because we also report  ${}^7\text{Li}/{}^6\text{Li}$ , the value of  $\alpha$  is the same as that reported by Chan et al.] A smaller  $\alpha$  of 1.003–1.007 at 350°C has been inferred from mid-ocean ridge hot springs [54]. The inferred temperature effect on isotope fractionation is comparable with results from the B isotope system, where experimental data are available (for a summary see [21,55]).

Evidence for moderate to high Li mobility (less mobile than B) has been demonstrated in mid-ocean ridge hydrothermal solutions [56], fluids sampled in subduction zone decollements [15,57] and hydrothermal experiments [1,2,3,58]. These inferences have been substantiated by experimental determination of Li partition coefficients between crystals and fluid ( $D^{\text{Min/Fluid}}$ ). Berger et al. [1] measured  $D^{\text{Min/Fluid}}$  of 1.7 for chlorites and 2.3 for smectites at 50°C. At 260°C, these values drop to 0.35 and 1.9, respectively. At 900°C and 2 GPa, Brenan et al. [3] determined  $D^{\text{Min/Fluid}}$  for clinopyroxene and garnet of 0.16 and 0.008, respectively.

During subduction, water is constantly released

from the hydrated basaltic crust by continuous and discontinuous reactions [59]. However, major fluid releases are caused by loss of interlayer water in clays (e.g. smectites) at ca. 100°C [60] and by the chlorite to garnet transformation at ca. 300–500°C. Both reactions involve Li-rich minerals, and, based on the  $D$  values given above, it is likely that Li is released to the fluid during these reactions.

The degree of isotope fractionation produced during dehydration reactions can be modeled by open-system Rayleigh distillation (for B see [21]), neglecting the possibility of kinetic complications during low- $T$  dehydration such as lack of equilibration between released water and surrounding minerals. The concentration of Li remaining in the solid ( $c_s$ ) is:

$$c_s = c_0(1-F)^{b-1} \quad (1)$$

where  $c_0$  is the Li concentration in the hydrated metabasalts,  $D$  the bulk partition coefficient for the dehydrated assemblage and  $F$  is the proportion of fluid removed [61]. For simplification, we assume that modal proportions do not change. The fraction of Li remaining in the rock ( $f = c_s/c_0$ ) is used to calculate the Li isotope composition in the remaining solid ( $\delta^7\text{Li}$ )<sub>s</sub> according to the Rayleigh distillation formulation [62]:

$$\delta^7\text{Li} = [(\delta^7\text{Li})_0 + 1000]f^{(\alpha-1)} - 1000 \quad (2)$$

For the altered oceanic crust we assume two idealized endmembers: (1) slightly altered basalt with 1 wt% H<sub>2</sub>O bound on the interlayer site of clays ( $F=0.01$ ), 15 ppm Li ( $c_0$ ) and  $(\delta^7\text{Li})_0$  of +5.5‰, and (2) highly altered basalt with 8 wt% interlayer-bound H<sub>2</sub>O, 80 ppm Li and  $(\delta^7\text{Li})_0$  of +14‰ (see Fig. 4 caption for details). The data for Trescolmen eclogites can be reproduced if the release of interlayer-bound water is modeled with a Li isotope fractionation factor ( $\alpha$ ) of 1.015 (interpolated for isotope fractionation at 100°C) and a Li partition coefficient between whole rock and fluid ( $D$ ) of 0.05. With the given partition coefficients, this can only be achieved if 2.5% Li-rich minerals (chlorite and smectite) remain.

As can be seen in Fig. 4, the result is that the more a basalt has been altered, corresponding to heavier  $(\delta^7\text{Li})_0$ , the lighter these rocks become

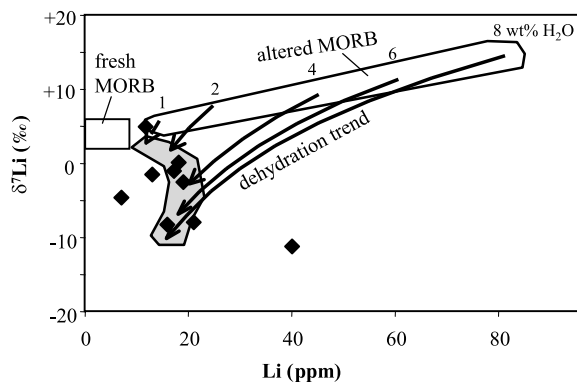


Fig. 4. Whole rock Li concentration and  $\delta^7\text{Li}$  of Trescolmen eclogites (black diamonds). Also shown is field for fresh MORB [4,9–11] and MORB altered at low temperatures [9]. Numbers next to altered MORB field are approximate wt%  $\text{H}_2\text{O}$  bound at interlayer sites of clays at corresponding Li concentration [44]. Rayleigh distillation was modeled according to Eqs. 1 and 2 with  $\alpha = 1.015$  and  $D = 0.05$ . Shaded field surrounds calculated compositions of altered MORB after Rayleigh distillation (see text for further explanation).

after dehydration. The dataset of Trescolmen eclogites is reproduced by these calculations in terms of (1) their light and heterogeneous  $\delta^7\text{Li}$ , (2) elevated Li concentrations compared to fresh MORB, and (3) a general correlation between the degree of alteration (based on the Na and K contents) and low  $\delta^7\text{Li}$  values (Fig. 2).

Spilitized basalts contain most of their water in chlorite, so isotope fractionation of samples with high  $\text{Na}_2\text{O}$  content (as a proxy for spilitization), like Z6-50-14, more realistically needs to be modeled by Rayleigh fractionation at temperatures of chlorite breakdown (at least  $300^\circ\text{C}$ ). Here, Li isotope fractionation is still effective, even with a reduced isotope fractionation factor ( $\alpha$ ) of 1.007 [54] if  $D^{\text{Rock/Fluid}}$  are kept low. Dehydration of 30% chlorite at  $300^\circ\text{C}$  corresponds to  $\text{H}_2\text{O}$  loss of 4 wt% (12 wt%  $\text{H}_2\text{O}$  in chlorite [60]). Under these conditions, reduction of  $\delta^7\text{Li}$  by as much as 14‰ can be achieved by adjusting the  $D$  value to 0.02 (high Li concentrations of 16 ppm remain in the dehydrated rock if 120 ppm Li are assumed in a highly spilitized protolith [47]). A low  $D$  value such as 0.02 is likely since chlorite breaks down during this reaction, producing garnet that does not favor Li [6,7,24].

We have not attempted to model the Li budget

of the metasediments due to insufficient data on experimental partition coefficients and fractionation factors for micas (dominant Li phase) and coexisting fluid. The metasediments lose less water during metamorphism than the metabasalts (modal abundance of phengite is ca. 40%, corresponding to 2.4 wt%  $\text{H}_2\text{O}$  in the schists) and this, coupled with a strong preference for Li in micas through the whole metamorphic cycle, may lead to limited Li mobilization and a restricted shift in the  $\delta^7\text{Li}$  values.

It has to be emphasized that the above model of Trescolmen eclogites is based on poorly-known parameters, such as  $\alpha$  and  $D^{\text{Min/Fluid}}$  for Li at variable temperatures. Therefore the exact results are subject to change, for example, the calculated  $D^{\text{Min/Fluid}}$  values can be higher (and less extreme) if  $\alpha$  is higher than assumed. However, the foregoing calculations clearly show the need for combining isotope fractionation *and* element partitioning.

## 6. Implications for Li recycling

Additional evidence for Li isotope fractionation due to dehydration of the subducting slab derives from fluids sampled in the decollement of the Costa Rica subduction zone [15] and from fluids associated with the Conical serpentine seamount [63]. In both cases the fluids with the lowest salinity and highest Li concentration (indicative of lowest seawater contamination) have  $\delta^7\text{Li}$  of about +20‰, considerably higher than the altered MORB and hemipelagic sediments from which they are derived ( $\delta^7\text{Li} \leq +12$ ‰ [15]). Fluids sampled at Conical seamount originate at a depth of ca. 25 km [64], and therefore have traversed the forearc mantle wedge. At low temperatures, mantle rocks in contact with fluid will form chlorite, serpentine and talc (for phase relations in the mantle forearc see [65]). Serpentine and chlorite have high concentrations of Li [66,67]. Beyond the stability field of these hydrous phases, the regular mantle minerals olivine, clinopyroxene and orthopyroxene can also store significant amounts of Li (ca 1 ppm [5,6], with up to 16 ppm Li reported in metasomatically enriched cli-



nopyroxene [7]). Thus, we predict that the forearc mantle wedge may form a sink for a high  $\delta^7\text{Li}$  component released from the dehydrating subducted oceanic crust (e.g. [17]).

During subduction the slab is progressively depleted in  $^7\text{Li}$ , with the extent depending on the original  $\delta^7\text{Li}$ , the amount of  $\text{H}_2\text{O}$  released and temperature of dehydration. As all these parameters are variable in subducting material, it is expected that the slab will be characterized by pronounced Li isotopic heterogeneity, similar to Trescolmen eclogites and garnet mica schists. In general, the most extreme Li isotopic fractionation in the basaltic crust is expected to occur in areas with the highest degree of alteration, like the uppermost section close to the seafloor and areas rich in breccias [45]. The amount of this material is believed to be around 20% in the upper volcanic section, with an average of 27 ppm Li in the breccia-rich areas at ODP 504B [13]. If the Trescolmen eclogites are broadly representative of dehydrated oceanic crust, then when the slab reaches depths beneath the volcanic front its average  $\delta^7\text{Li}$  will be less than or equal to that of unaltered MORB. Since mineral–fluid fractionation at these

temperatures will probably be small (with the caveat that *no* experimental data exist), the Li isotopic signature of fluid or melt released from such rocks will be predominantly lighter than MORB. However, since ca. 90% of all analyzed island arc volcanic rocks have a mantle-like  $\delta^7\text{Li}$ , the Li budget in most island arcs is probably buffered by the mantle [17].

Of the 10% of known arc rocks having  $\delta^7\text{Li}$  different from MORB, most are isotopically heavier. Our data suggest that these high  $\delta^7\text{Li}$  volcanic rocks (up to +11.2‰ in Panama [16]; up to +7.6‰ in Izu arc [10]; up to +7.4‰ in Kurile arc [17]; up to +6.4‰ in Costa Rica [18]) cannot be explained by direct fluid addition from the slab, which appears to be light beneath the volcanic front. Instead, forearc mantle, enriched in  $^7\text{Li}$  from the dehydrating slab, may be incorporated into the source region of island arc magmas under certain conditions. This could occur either by downward transport of metasomatized forearc mantle [22,68] or by incorporation of forearc mantle into arc source regions by intra-arc rifting [69]. In either case, the forearc mantle wedge was metasomatized by time-integrated fluid flux from

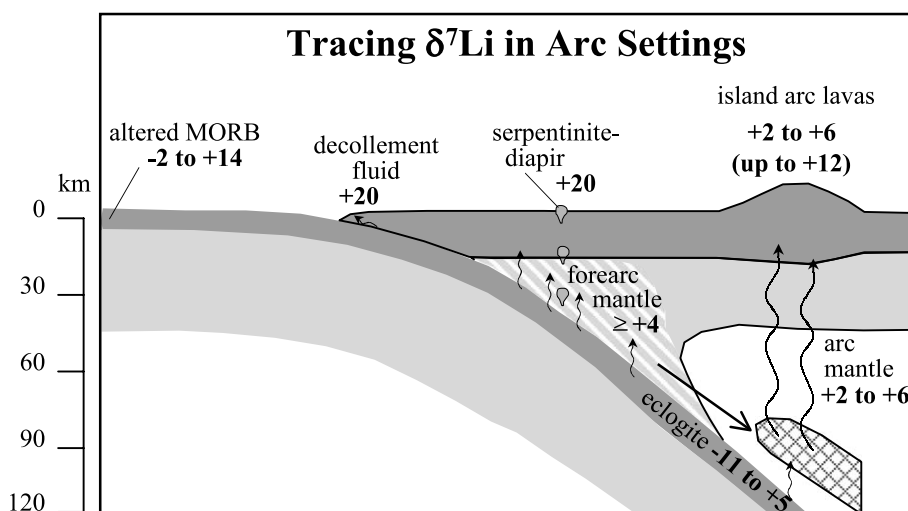


Fig. 5. Schematic illustration of Li isotope systematics in a subduction zone setting. Li isotopic fractionation during dehydration of altered MORB (+3 to +14‰) is evidenced by heavy Li in fluids from decollement zone and serpentinite diapir (both +20‰) and by light Li in eclogites (–11 to +4‰). The high  $\delta^7\text{Li}$  of fluids escaping the slab at low temperatures likely enriches the forearc mantle wedge in  $^7\text{Li}$ . Assuming  $\delta^7\text{Li}$  of island arc magmas represent the composition of the mantle underneath them (cross-hatched region), large parts of the subarc mantle appear to be unaffected by slab Li (+2 to +6‰). High  $\delta^7\text{Li}$  values in some arc magmas (up to +12‰) might be explained by the incorporation of the forearc mantle into the subarc mantle region.

water released early in the dehydration of the slab (Fig. 5).

A direct implication of this study is the likelihood that subducted slabs are recycled into the mantle with Li isotopic compositions lighter than normal MORB. This isotopically light component might eventually be sampled by plume activity [70], as suggested by Tomascak et al. [16]. If so, one might expect to find  $\delta^7\text{Li} < \text{MORB}$  in hot spot-related ocean island basalts (OIB). The sparse Li isotope data from various hot spots available to date [71,72] are mostly MORB-like; the lightest sample (+1.4‰ from Erebus [71]) is not significantly lighter than the accepted mantle range. More data on OIB are desirable before we can evaluate the utility of Li isotopes in tracking subducted oceanic crust.

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