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# The terrestrial Li isotope cycle: light-weight constraints on mantle convection

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## Abstract

The two stable isotopes of Li are significantly fractionated by exchange reactions with clays near the Earth's surface. The isotopic legacy of this process provides a robust tracer of surface material that is returned (recycled) to the mantle. Altered oceanic crust has a heavy Li isotopic composition (high  $^7\text{Li}/^6\text{Li}$ ). Heterogeneous distribution of subducted, altered oceanic crust in the mantle will result in variations in Li isotope ratios. A rapidly accumulating dataset of Li isotope analyses on mantle-derived materials indeed indicates a significant range in Li isotope ratios. This observation provides powerful evidence for the widespread distribution of recycled material in the convecting mantle. There is substantial overlap in Li isotopic compositions of ocean island basalts (OIB) and mid-ocean ridge basalts (MORB). Some OIB, however, have slightly heavier Li compositions than typical, depleted MORB. At face value this suggests a larger contribution of recycled oceanic crust in the sources of some OIB than in the upper mantle. Yet recent evidence implies that heavy Li is lost from the slab at subduction zones and the recycled residual crust is left with an isotopically light signature. Extremely light Li isotope ratios are observed in some continental mantle xenoliths but not in OIB proposed to contain large proportions of recycled crust. Studies of subduction zone lavas imply the heavy Li isotope signature of altered oceanic crust is transferred to the mantle above the subducting plate. Thus cycling of sub-arc mantle may be an important process in forming chemical heterogeneities sampled by OIB. Inferences from initial Li isotope results are thus notably different from those from the longer established but more equivocal radiogenic isotope tracers. Li isotopes promise to provide significant new constraints on the distribution of recycled material in the mantle and its implications for mantle convection.

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## 1. Introduction

Mantle convection stirs the Earth's interior. Understanding this first-order planetary process has been improved by increasingly sophisticated fluid dynamic models [1] and better resolved seismic images of the mantle's velocity structure [2]. It is also necessary to develop in tandem geochemical tracers of convection. The importance of geochemistry is that it provides a time-integrated signal of the effects of convection and can trace the fate of material with distinctive compositional signatures. In partnership with the complementary present-day picture from seismology, geochemistry provides the observables for convection model testing [3,4].

The formation and subduction of oceanic plates is an inherent part of mantle convection. The return to the mantle of oceanic crust (and its depleted residue), variably influenced by its near-surface residence, is frequently termed 'recycling'. Determining how recycled material is distributed in the present-day mantle informs on the style of mantle convection. In seeking this elusive goal, a number of isotope systems have been employed as tracers of recycled plates. Radiogenic isotope systems are most commonly used (e.g. [3,4]), but can be strongly influenced by processes other than oceanic crustal formation, alteration and subduction. Although many popular interpretations of radiogenic isotope variations implicitly invoke recycled material, the evidence is equivocal [5].

Stable isotope tracers are highly desirable to ground-truth inferences from radiogenic isotopes. Stable isotope fractionation is dominantly the result of low-temperature processes near the Earth's surface. Thus significant variations in the stable isotope ratios of mantle-derived samples unambiguously reflect variable contributions of recycled material. This logic has prompted a careful re-examination of the oxygen isotope signatures of mantle-derived basalts using high-precision laser fluorination techniques (see [6], for recent summary). Such oxygen isotope studies have identified some lavas that clearly contain recycled material in their source [7]. Yet most mantle-derived melts show a rather small range in oxygen isotope compositions. Whilst this may reflect a lack of

recycled input, it may also reflect a lack of sensitivity of oxygen isotopes to some recycling processes.

Here we highlight the potential of the Li isotope system in tracking the fate of subducted material and its distribution by mantle convection. We initially summarise the behaviour of Li isotopes in the near-surface environment to understand the controls on Li isotope fractionation. We then consider the effects of subduction zone processes on the Li isotope systematics of the altered oceanic crust. Finally we assess the burgeoning, but still modest, Li isotope data on mantle-derived samples. Li isotope geochemistry is a juvenile research area, dominated by work in the last decade. Systematic study of the Li isotope ratios of mantle-derived rocks is even more immature. Thus we can only present a tantalising aperitif of work that may follow and note that our interpretations are still at the frontier stage.

## 2. Preliminaries

Lithium has two stable isotopes, 6 and 7, which have the biggest relative mass difference of any isotope pair aside from hydrogen–deuterium. The potential for mass-dependent fractionation is thus obvious. Unlike the better established light stable isotope systems (e.g. C, O, S), Li is a trace cation and does not form an integral part of hydrological, atmospheric or biological cycles. Hence measurements of Li isotopes are likely to provide rather different information than is available from the more commonly used isotope systems.

As with other stable isotope measurements, Li isotope ratios are typically expressed in a delta notation:

$$\delta^7\text{Li} = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}} / ({}^7\text{Li}/{}^6\text{Li})_{\text{standard}} - 1] \times 1000$$

where the standard is conventionally the National Institute of Standards highly purified  $\text{Li}_2\text{CO}_3$  reference material NIST L-SVEC [8] which has  ${}^7\text{Li}/{}^6\text{Li} \approx 12.15$  [9]. As has occurred in the early stages of development of other isotope systems, some confusion has arisen over the form in which data are reported. Both  $\delta^7\text{Li}$  and  $\delta^6\text{Li}$  have been

used in the literature, but increasingly the  $\delta^7\text{Li}$  notation has become standard (e.g. [10]). In the  $\delta^7\text{Li}$  formulation, more positive values are also isotopically *heavier*, in keeping with other stable isotope systems. Measurements reported as  $\delta^6\text{Li}$  can be readily converted to  $\delta^7\text{Li}$ . Simply changing the sign of  $\delta^6\text{Li}$  measurements yields a value that generally closely approximates the corresponding  $\delta^7\text{Li}$ .

Measurements of Li isotope ratios have traditionally been made using thermal ionisation mass spectrometry [11–13]. Although Li is efficiently ionised by solid source mass spectrometers, highly reproducible isotope ratios are more difficult to obtain by this technique than for the gas-source machines used to measure oxygen isotopes. The reproducibility of Li isotope measurements has thus lagged behind oxygen isotope measurements, typically  $\sim 1\%$  compared to  $\sim 0.05\%$  (all errors in this contribution are cited as  $2\sigma$  standard deviations). This has hampered application of Li isotopes to studying mantle processes, where variations in Li isotope ratios are only a few per mil (see below), but it has been sufficiently precise for documenting the larger isotopic variations in the near-surface environment. Thermal ionisation measurements are also time-consuming and so the Li isotope database has remained relatively limited. The advent of plasma ionisation multi-collector mass spectrometry has allowed a considerably faster throughput of smaller samples [14,15]. New-generation plasma ionisation multi-collector mass spectrometers have also enabled a major improvement in reproducibility, typically  $\pm 0.2\%$  [16], much closer to oxygen isotope measurements and better than the best thermal ionisation data ( $\pm 0.5\%$ ) [10]. This advance is highly significant for documenting Li isotopic variations in the mantle.

### 3. Behaviour of Li in the hydrological cycle

The fractionation of Li isotopes is dominated by partitioning of Li between clays and water [17–21]. It is important to review briefly the fundamentals of these low-temperature processes in order to understand the potential of Li isotopes as a

tracer of subducted material. This pioneering work of Chan and co-workers in the last decade has laid the essential foundations for exploiting Li isotopes as high-temperature tracers [17,22,23]. Readers interested in more detail on this and other aspects of Li geochemistry are referred to a recent and comprehensive review by Tomascak [24].

Weathering of the continents both releases Li and isotopically fractionates it [23]. Minerals are characteristically enriched in  $^6\text{Li}$  relative to co-existing aqueous fluid [21,25]. Thus river waters have heavy Li isotope compositions compared to the original bed-rock and associated suspended load [20]. The Li isotopic composition of river water is not highly sensitive to the Li isotope composition of the bed-rock of the catchment area, in contrast to some radiogenic isotope ratios used to monitor chemical weathering [23]. There is thus promise in using the evolution of the Li isotope ratio of seawater to assess past changes in the intensity of continental weathering, with its attendant implications for atmospheric  $\text{CO}_2$  and long-term climate change (e.g. [26]). In a simplistic scenario it might be anticipated that a change to lighter Li isotope compositions in ancient oceans would reflect lower weathering rates in the past. Whilst the general process of Li isotopic fractionation at the surface is clear, a more detailed understanding of the behaviour of Li isotopes during weathering, transport and incorporation into the geological record is required before Li isotope ratios can be used as weathering proxy (for recent review on chemical proxies of past conditions see [27]). However, an increasing number of groups are investigating this potential and this is an exciting prospect for the future [21,28–32].

In the marine system too, partitioning of Li between water and clays results in major isotopic fractionation [17,18,25]. This results in an initially puzzling observation. Unlike radiogenic isotope systems, such as  $^{87}\text{Sr}/^{86}\text{Sr}$ , where seawater represents a intermediate mix of a hydrothermal input (unradiogenic, mantle-dominated signature) and river water (radiogenic, continental signature), seawater has a Li isotope ratio heavier than its inputs (Fig. 1). This paradox is explained by the

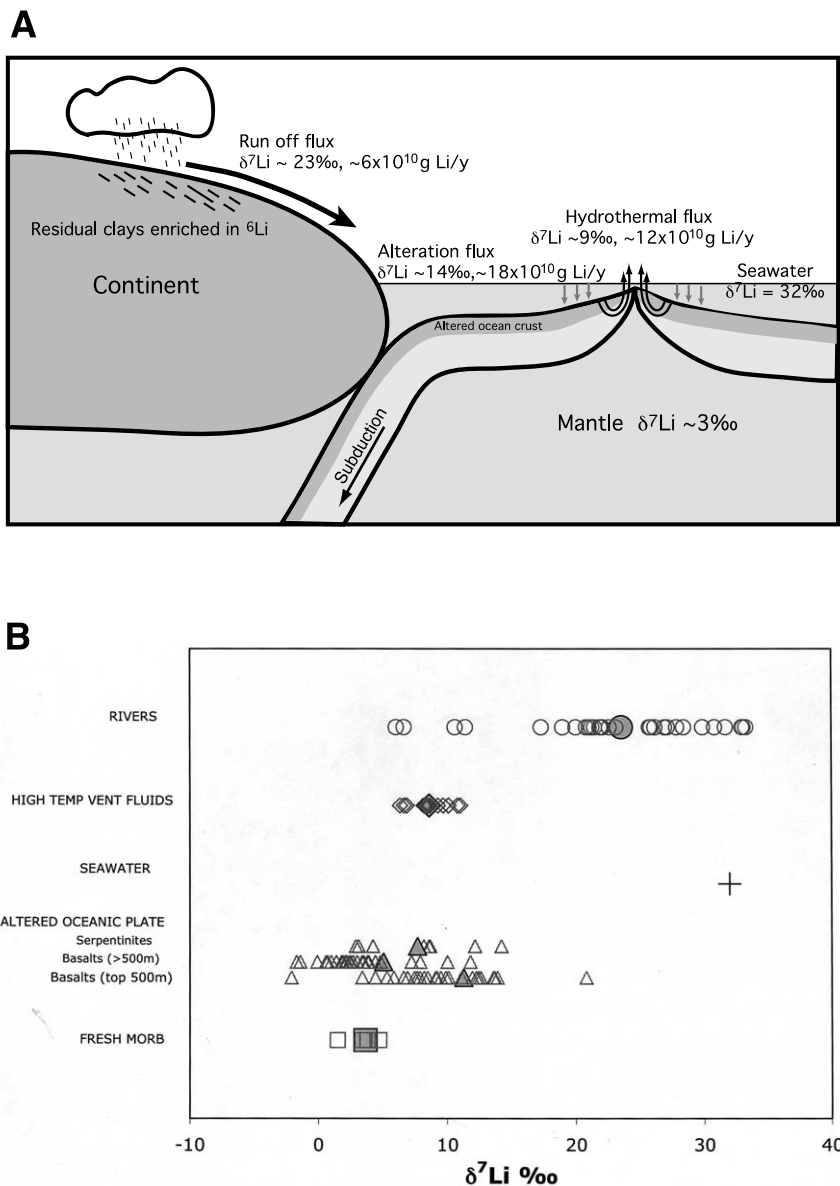


Fig. 1. (A) Cartoon of the main fluxes that control Li isotope mass balance in the oceans. Flux estimates taken from [23]. (B) Analyses that constrain the ocean Li isotope mass balance. Individual analyses are shown as open symbols with weighted means indicated by larger symbols. Typical uncertainties are  $\pm 1\text{‰}$ . Data sources: rivers [23], high-temperature vents [22], seawater compilation from [13], fresh MORB [17,34]. The oceanic plate is divided into three stratigraphic components to illustrate the upper (top 500 m), high- $\delta^7\text{Li}$ , low-temperature altered basalts [17,33]; lower (> 500 m) basalts, some of which represent the light residue of high-temperature hydrothermal fluids (note these are also depleted in Li and only weakly affect the weighted mean of this section) [33]; serpentinised upper mantle [74]. The low-temperature altered basalts have strongly elevated Li concentrations and dominate the Li isotope budget of the altered crust.

low-temperature alteration of the oceanic crust to hydrous minerals (such as smectite and phillipsite). These alteration products are important sinks for oceanic Li and also preferentially remove  $^6\text{Li}$  from seawater during this process [17,33]. Enhanced removal of  $^6\text{Li}$  from the oceans results in a complementary, heavy seawater composition of  $\delta^7\text{Li} \approx 32$  (e.g. compilation in [13]), heavier than its average input. Although the Li gained by the alteration material is lighter than mean river water,  $\delta^7\text{Li} < 23\text{‰}$  [23], it is nevertheless heavier than fresh oceanic basalts,  $\delta^7\text{Li} \approx 3$  [17,34].

In summary, weathering of silicates on the continents produces river water with isotopically heavy Li which feeds the oceans. Low-temperature alteration of oceanic crust serves to make seawater even heavier than river water. Even though altered oceanic crust is isotopically light compared to mean river water, it is notably heavier than mantle values (Fig. 1B).

The process of increasing the  $\delta^7\text{Li}$  of altered oceanic crust as part of the low-temperature Li cycle thus imparts a distinctive signature to the oceanic plate that can be used to trace it. We first, however, assess if the magnitude of this heavy, recycled flux is sufficient to affect the Li isotopic composition of the mantle as a whole. The flux might seem most straightforwardly calculated by using an estimate for average altered oceanic crust and present-day rates of plate subduction. Although it is clear that altered oceanic crust is heavy [17,33], Li isotope analyses of altered oceanic crust are only available from a few localities worldwide. Only three samples have been analysed that are older than 10 Myr. Constructing a representative value for average altered oceanic crust that has experienced a full range of alteration processes is therefore difficult. Thus we prefer to estimate the net Li isotope flux to the oceanic crust, and ultimately the subduction zone, indirectly by examining the Li isotope mass balance in the oceans. Using the commonly made assumption of a steady-state seawater composition, the Li isotope flux to the altered oceanic crust must balance the input flux from rivers and hydrothermal vents. Since the hydrothermal flux is itself dominantly derived from the oceanic crust itself,

the net flux to the oceans equals the riverine flux of  $\sim 6 \times 10^{10}$  g/yr with  $\delta^7\text{Li} = 23\text{‰}$  [23].

The ramifications of returning this flux of heavy Li to the mantle via subduction of the altered oceanic crust are explored in Fig. 2. It is evident that the magnitude of the recycled flux is just sufficient to influence the composition of the mantle as a whole. Moreover, if recycled material is not efficiently mixed throughout the whole mantle it can significantly change ( $\sim 1\text{‰}$ ) the Li isotope composition of a more restricted portion of the mantle, e.g. the upper mantle (Fig. 2). The relative Li isotopic compositions of different mantle reservoirs thus have clear implications for assessing the style of mantle convection.

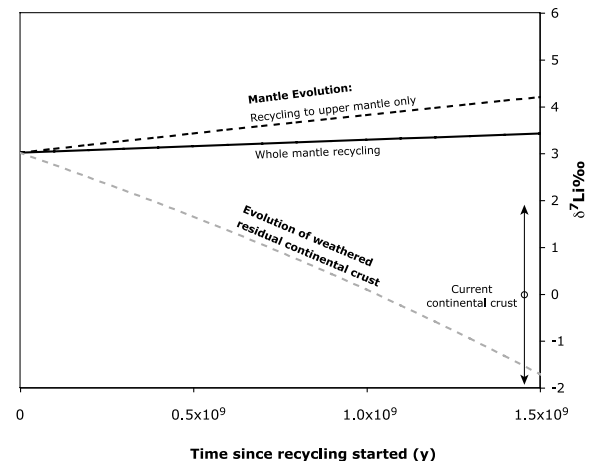


Fig. 2. Li isotopic evolution of crustal and mantle reservoirs in response to weathering and subduction of Li. The simplistic model illustrates the cumulative effect of removing the riverine Li flux ( $5.6 \times 10^{10}$  g/yr,  $\delta^7\text{Li} = 23\text{‰}$  [23]) from the continental crust and adding it to the mantle via subduction. The graph shows the effects of two scenarios: adding the subducted flux to the whole mantle ( $4 \times 10^{27}$  g) and just upper mantle ( $1.33 \times 10^{27}$  g). Both reservoirs are initially assumed to have  $[\text{Li}] = 1 \mu\text{g/g}$  and  $\delta^7\text{Li} = 3\text{‰}$ . The continental crust ( $2 \times 10^{25}$  g) is assumed to have an initial  $\delta^7\text{Li} = 3\text{‰}$  (since it is ultimately derived from the mantle) and  $[\text{Li}] = 22 \mu\text{g/g}$  [35]. Each reservoir is assumed to be homogeneous and therefore changes are averaged over the whole reservoir. The model is run in  $1 \times 10^8$  yr time steps for  $1.5 \times 10^9$  yr. After this time, the composition of the model continental crust composition is at the lower end of continental composites analysed by [35] and so the model is run no further. The composition for current continental crust is from [35], illustrating a preferred average for whole crust and 1 standard deviation of all upper crustal samples measured.

The increase in  $\delta^7\text{Li}$  of the mantle sketched in Fig. 2 ultimately results from weathering of the continents, followed by cycling heavy Li through the oceans and altered oceanic crust into the mantle. Continental crust is originally derived from the mantle and these two reservoirs should initially have had the same Li isotope ratio. Continued addition of heavy Li into the mantle by subduction must have a complementary effect on the Li isotope ratio of the continents. The Li isotope composition of the continental crust thus provides an important constraint on how heavy the mantle can have become through time. Valuable recent studies report a light Li isotopic composition ( $\delta^7\text{Li} \approx 0$ ) for both the upper [35,36] and lower [37] continental crust with a mean  $[\text{Li}] = 22$  ppm [35]. The light Li isotope ratio of the present-day continental crust can be produced in only 1 Gyr of recycling at current rates. This suggests that the recycled Li flux calculated from present-day oceanic mass balance may be anomalously high, possibly as a result of enhanced current weathering rates from Himalayan uplift (e.g. [26]) or simply due to inaccuracies in the approach. Regardless of the rate at which the continents have become light, however, the Li isotope composition of the continental crust limits the change in the  $\delta^7\text{Li}$  of the whole mantle to be  $\sim 0.3\%$ .

Before considering how subduction modifies the Li alteration flux into the mantle it is worth briefly contrasting the Li isotope signature of altered oceanic crust with longer established measurements of oxygen isotopes. Oxygen is nearly equally abundant in most silicate rocks, from clays to mantle minerals, whereas altered upper oceanic crust has a Li concentration some 10 times greater than the mantle. Recycling of altered oceanic crust to the mantle will thus have a greater leverage on the Li isotope system. Moreover, heavy oxygen isotope ratios in the upper oceanic crust are compensated by light oxygen isotope ratios in the lower oceanic crust [38]. Thus the oxygen isotopic composition of the complete sequence of altered oceanic crust is the same as pristine mantle. Nevertheless, oxygen isotopes have provided striking evidence for the presence of specific portions of recycled crust in some ocean island basalt (OIB) sources, notably sedi-

mentary material [39] and lower portions of the altered oceanic crust [40]. Yet oxygen isotopes are insensitive to the wholesale addition of altered oceanic crust to a mantle source. Interpretation of the similarity of most peridotite, mid-ocean ridge basalt (MORB) and OIB oxygen isotope ratios [7] is therefore ambiguous.

#### 4. The subduction zone filter

Plate tectonics inevitably mixes altered oceanic crust, with its budget of heavy Li, back into the mantle. However, the passage of Li from the surface to depth is not simple and is strongly affected by the processes occurring during subduction (Fig. 3A). Water is successively lost during subduction, first through porosity reduction during compaction and then through a series of prograde dehydration reactions as the descending slab becomes hotter (e.g. [41,42]). As in the near-surface environment, the partitioning of Li between residual solid and liquid will result in isotopic fractionation. Although isotopic fractionation diminishes with increasing temperature, there is still significant inferred [22,33] and measured [25] Li isotopic fractionation between mineral phases and water during high-temperature hydrothermal circulation at  $\sim 350^\circ\text{C}$ . Thus the potential for isotopic fractionation extends well into the subduction zone.

Fluid is expelled out of the subduction zone as a result of compaction of the sedimentary pile. These fluids that return to the ocean along the so-called décollement are isotopically heavier than the associated sediments [19]. Further insight into the shallow subduction zone is provided by serpentine diapirs which sample the highly hydrated fore-arc. Analyses of Mariana serpentinites show a wide range of  $\delta^7\text{Li}$  from light ( $-0.5\%$ ) to heavy values ( $+10\%$ ) [43], although finer-grained fractions show dominantly heavier values ( $\delta^7\text{Li}$  5–9%) [44]. Thus some of the heavy subducted Li is clearly lost to the oceans and shallow wedge, but the amount of Li lost from the slab in these early dehydration processes is estimated to be a minor fraction of the total Li subducted [19,45]. In contrast, the budget of B is significantly de-

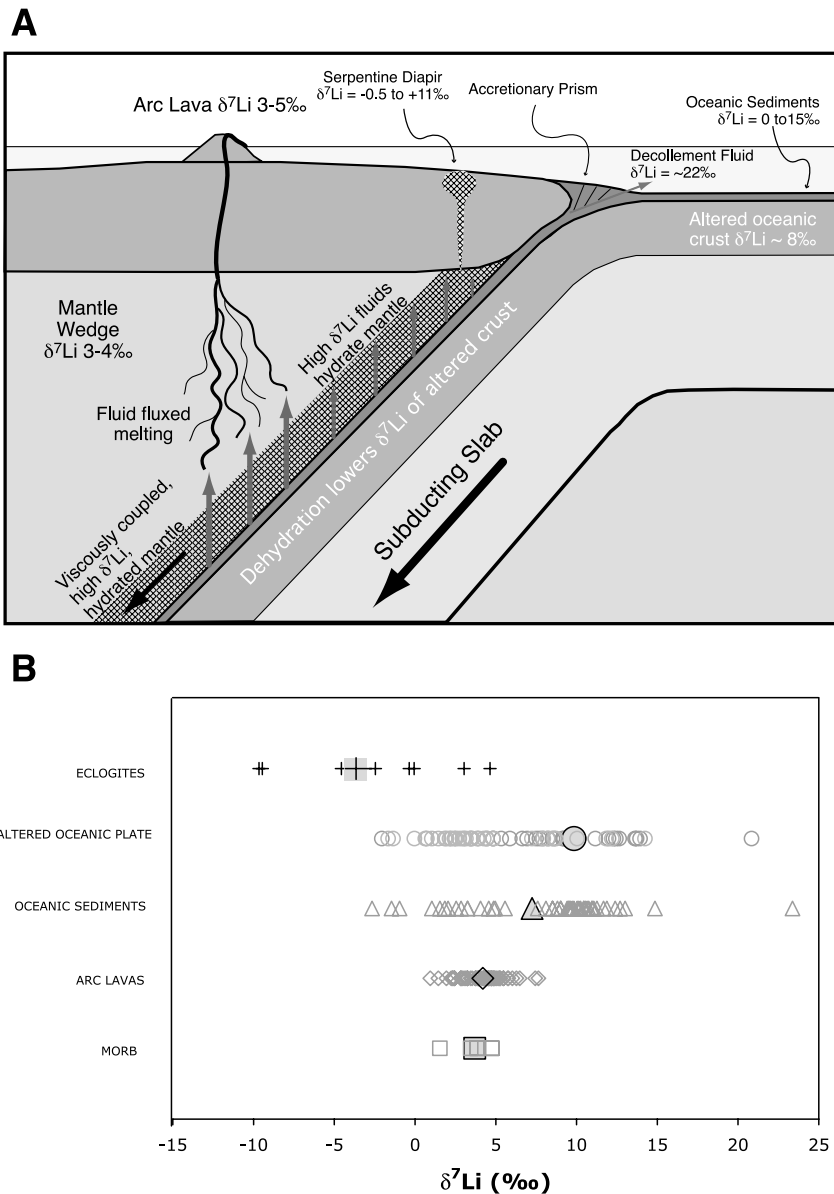


Fig. 3. (A) Cartoon of the Li isotope behaviour in the subduction zone, illustrating processes discussed in the text. Sketch indicates transfer of fluids with heavy Li to hydrate the adjacent mantle (hatched). The hydrated mantle is viscously coupled and down-dragged with the complementary, isotopically light, dehydrated oceanic crust. Fluids that traverse into the hotter interior mantle wedge and induce melting have already isotopically equilibrated their Li with the preceding mantle. Thus arc lavas have  $\delta^7\text{Li}$  comparable to the pristine mantle wedge. (B) Li isotopic composition of inputs and outputs from subduction zone. Individual data are shown with weighted means represented as larger symbols. Note that despite the heavy mean compositions of both incoming sediments and altered ocean crust, the vast majority of arc lavas have  $\delta^7\text{Li}$  within error of MORB (uncertainties for most arc measurements  $\pm 1\text{‰}$ ). Samples sources: eclogites [52], altered oceanic crust (see Fig. 1), oceanic sediments [18,19,34,49,75], arc lavas [34,48,49,76]. The older Panama samples reported in [76] are not plotted due to the possible effects of 10 Myr of weathering in a tropical environment, which can increase  $\delta^7\text{Li}$  of samples [10].

pleted by fore-arc dehydration [45,46] which compromises its potential as a tracer of recycled material.

A major mass flux at subduction zones is associated with magmatism at the volcanic front. Subduction zone magmas are characterised by some distinctive chemical signatures. Notably arc lavas have elevated concentrations of elements empirically observed to be mobile in aqueous fluids (such as Li) relative to elements that form highly charged ions and have low solubilities in aqueous fluids (e.g. Y) but otherwise behave similarly during magmatic processes (for a recent review see [47]). Thus arc lavas have high Li/Y ratios (e.g. [48]). Analogous ratios, such as Ba/Th, have long been used to implicate the addition of aqueous-rich fluids from the down-going slab to the source of arc lavas (in the mantle wedge). The elevated Li/Y of arc lavas would hence be anticipated to be associated with heavy Li, fluxed from the subducting slab. It is surprising that very few arc lavas have Li isotope ratios significantly heavier than MORB [48] (see Fig. 3B). Two studies of arc lavas show variations of Li isotope ratios with some key trace element ratios, suggesting a trend to heavier Li ratios with larger slab-derived inputs [34,49]. Such systematic variations are not observed, however, in comprehensive studies of a number of other arcs ([48], Bouman, unpublished data).

That few arc lavas have heavy Li isotope ratios implies that little of the budget of heavy Li that enters the subduction zone is lost to the surface as a result of arc magmatism. Yet, as discussed above, several ‘fluid-mobile’ tracers of the slab are evident in arc lavas. The lack of an associated heavy Li isotopic signature can be related to the relative affinity of Li for mantle phases. Li has an ionic radius comparable to Mg and can occupy the abundant Mg lattice sites available in the mantle. Although apparently preferentially transported by fluids, high-temperature partitioning experiments show that Li is only moderately incompatible in either melt or fluid relative to mantle phases [50,51]. Thus it is likely that heavy Li initially carried from the slab in aqueous fluids isotopically re-equilibrates with the mantle [48]. The heavy Li isotopic signature from the slab is effec-

tively transferred to the cold portion of mantle lying above the slab (Fig. 3A).

Striking evidence for the loss of heavy Li from the subducted oceanic crust itself is found in the extremely light Li isotopic ratios ( $\delta^7\text{Li}$  as low as  $-11\%$ ) of Alpine eclogites [52] (see Fig. 3B). These high-pressure metamorphic rocks are believed to be fragments of deeply subducted oceanic crust that have been rapidly exhumed by thrusting during the Alpine orogeny. Zack et al. [52] argue that the loss of Li during pro-grade metamorphism during subduction is associated with significant isotopic fractionation. As in the surface environment, Li in the fluid phase is enriched in the heavy isotope leaving the dehydrated slab isotopically light. If accumulated effects of dehydration are modelled as a Rayleigh distillation process, the final ‘anhydrous’ residue at the end of subduction zone processing can have extremely light Li isotope ratios. This mechanism can be invoked to account for the very light Li isotope ratios observed in the eclogites (see Fig. 3B). Comparable isotopic fractionation during subduction has been noted in the boron isotope system [53–55]. The Alpine eclogites thus represent the light complement of the heavy isotopic signature that has left the slab to reside in the overlying, viscously coupled mantle.

The effects of subduction thus provide additional interest in the use of Li isotopes as tracers of mantle convection. The deep recycled, dehydrated altered oceanic crust becomes isotopically light. Meanwhile the cool mantle adjacent to the slab becomes heavy. Thus we have two inputs to the mantle as a result of subduction that are isotopically distinct from the mantle itself. Moreover, since these are stable isotope variations, these signatures can be unambiguously linked to low-temperature processes near the surface of the Earth. Li isotopes therefore provide a means to trace the mixing of subducting slab and adjacent mantle wedge back into the convecting mantle. It is of great interest to see how Li isotope signatures of recycling compare to radiogenic isotope measurements. Although the latter have long been used to infer the distribution of recycled material, their variations can be interpreted in other ways and are much more equivocal.



## 5. Mantle signatures

MORB and OIB represent our primary sample of the mantle (for a review see [56]). The melting process averages melts from a large volume of source rock and so studying melts is an efficient approach to sample the mantle. MORB are the product of shallow (dominantly less than 60 km) decompression melting in response to plate spreading. MORB thus effectively sample the ambient shallow mantle. OIB are thought to be derived from melting of mantle that is hotter, or with a low solidus, such that it commences melting deeper than MORB mantle. Thus OIB can be generated by upwelling even beneath thick oceanic lithosphere. The upwellings required to produce OIB are frequently attributed to mantle plumes. Since plumes need to be sourced at a major thermal boundary, most appealingly the core–mantle boundary, they are generally thought to sample deeper mantle than the source of MORB.

OIB are typically more ‘enriched’ than MORB, with higher incompatible element contents and isotope ratios that reflect long-term elevation of more incompatible relative to less incompatible elements (e.g. high  $^{87}\text{Sr}/^{86}\text{Sr}$ ). Maintaining this contrast in geochemical signatures between MORB and OIB sources is an important constraint on mantle convection models [3,4,57,58]. The nature of the ‘enrichment’ in different OIB is not uniform and several end-member compositions have been identified. The role of recycled material has long been invoked to account for several of these end-member compositions. In a popular general scenario, manifest in a variety of different specific forms (see [59]), a deep mantle layer is fed by subducted plates and ultimately forms the source for OIB. From the behaviour of Li in the subduction zone discussed above, this lower mantle layer would likely evolve with a lighter Li isotope ratio than the upper mantle. Thus OIB might be expected to have a lighter Li isotope ratio than MORB. This should be particularly marked for the so-called HIMU OIB which are argued to have a large portion of recycled mafic crust in their sources (see [56]).

Before examining the Li isotope data for oceanic basalts, several important caveats need to be

addressed. Whilst variations in stable isotope ratios in mantle-derived rocks represent the least ambiguous signal of the (variable) presence of material that has been affected by processes close to the Earth’s surface, it is vital to assess if this is from deep recycled material or simply shallow-level contamination during magmagenesis [60,61] or even recent weathering [10]. Conclusively ruling out a role of crustal assimilation is difficult, but the potential effects can be minimised by analysing relatively ‘primitive’ samples. In the case of Li, it is possible to measure the isotope ratio of the early crystallising phase olivine, which should be least affected by contamination processes. The ability to analyse olivines is also an asset in studying older samples where identification of possible alteration in the whole rock is difficult [10]. Fresh olivines can be readily picked from many OIB in the same way that fresh glass can be prepared from MORB to produce reliable sample material. Although fractionation of stable isotopes is diminished at high temperatures, it is important to quantify the possible isotope fractionation induced by magmatic processes. Neither variable melting [62] nor basaltic differentiation processes [63], however, appear able to generate significant variations in Li isotope ratios.

Li isotope data remain sparse for samples from our planet’s interior. In the case of MORB, there are only six measurements of fresh samples in the literature and these range in  $\delta^7\text{Li}$  from 1.5 to 4.7‰ [17,34]. Five of these six measurements range from 3.2 to 4.7‰, which is within error of the techniques used in these analyses. A recent high-precision study ( $\pm 0.3\%$ ) of hand-picked, fresh glasses from the East Pacific Rise (EPR) yields a range of  $\delta^7\text{Li}$  of 3.1–5.2‰ [64]. Significantly, the Li isotope compositions in this study correlate with radiogenic isotope and highly incompatible element ratios. Covariation of Li isotopes with  $^{143}\text{Nd}/^{144}\text{Nd}$ , for example, makes contamination an unlikely explanation for the range in Li isotopes. The EPR dataset supports other unpublished studies that argue for a ‘depleted’, N-MORB  $\delta^7\text{Li}$  of 3–4‰ [17,65] and significant Li isotope variations within MORB globally [66].

The spread of  $\delta^7\text{Li}$  in MORB data requires recycled material to be mixed variably back into the

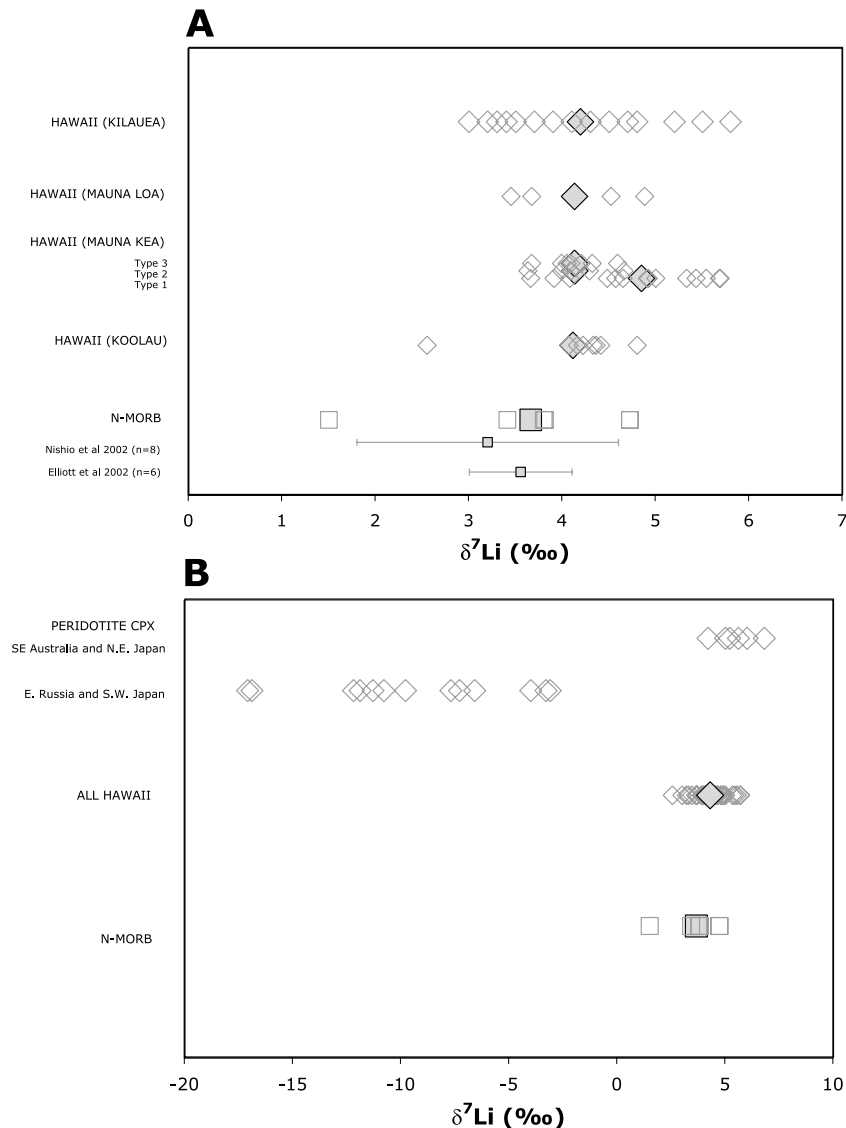


Fig. 4. (A) Li isotopic compositions of all published MORB [17,34] and Hawaiian lavas [10,13,21,63]. The published MORB samples are all N-MORB (depleted compositions) and can be compared with other unpublished N-MORB averages [64,65]. The Hawaiian samples have uncertainties of 0.5‰, except for Kilauea where measurements have errors of  $\sim 1\%$ . MORB samples likewise have errors of  $\sim 1\%$  apart from the analyses of [64] which have a reproducibility of  $< 0.3\%$ . Some of the Hawaiian samples reported in [10] are altered and we have only plotted samples that have K/Rb ratios that fall within the range of 380–630, cited as representative of pristine samples [10]. The samples from Mauna Kea have been sub-divided into types 1–3 that display distinct chemical signatures and variable contributions from different source components (see [10]). (B)  $\delta^7\text{Li}$  of clinopyroxenes from several mantle nodule localities [71] compared to MORB and Hawaiian data reported in A.

upper mantle. This has long been proposed as a logical conceptual corollary of plate tectonics [67]. Yet only very recently has the first unequivocal evidence of this process been presented, in the

form of subtle variations in oxygen isotope ratios [68]. The Li isotope data provide strong additional support to this idea.

Li isotope analyses of OIB are also scarce. An

important OIB datum is that of the international standard BHVO, a recent eruption from Hawaii. It is well established that this basalt has  $\delta^7\text{Li} > 4.7\text{‰}$  [10,13,21] and so is *heavier* than N-MORB. This lonely data point has been considerably augmented by further analyses from Hawaii [10,63] (see Fig. 4A). The latter study is at higher precision ( $\pm 0.5\text{‰}$  compared to typical  $\pm 1\text{‰}$  of previous studies) and also includes analyses of the older Koolau lavas. The Koolau lavas are remarkable for an enriched, heavy oxygen isotope component in their source, clearly implicated as sedimentary in origin [39]. Additionally samples from Mauna Kea can be sub-divided into groups that reflect different proportions of distinct components in their sources. For example, the type 1 lavas have high  $\text{SiO}_2$  and have been argued to contain recycled, mafic oceanic crust whereas type 3 lavas, with the highest  $^3\text{He}/^4\text{He}$ , contain the largest proportion of ‘undegassed’ mantle.

There is considerable overlap between the  $\delta^7\text{Li}$  of MORB and Hawaiian lavas (Fig. 4A). Nevertheless, the Hawaiian lavas are on average heavier than N-MORB. Despite the notable geochemical contrasts between the different Hawaiian compositions (Koolau and various Mauna Kea types) their differences in  $\delta^7\text{Li}$  are subtle. It is worth noting, however, that the Mauna Kea lavas invoked to contain the largest component of recycled mafic, oceanic crust (type 1) have heavier  $\delta^7\text{Li}$  than the other lava types. This is in keeping with unpublished data [69,70] that document heavy Li isotope ratios (5–7‰) in end-member ‘HIMU’ lavas, which are traditionally thought to contain large amounts of recycled mafic oceanic crust [56].

Recent analyses of clinopyroxenes from mantle nodules [71] provide an exciting counter-poise to the data from mantle-derived lavas (Fig. 4B). Whilst some samples have  $\delta^7\text{Li}$  that overlap OIB values, the clinopyroxenes from Far East Russia and southwestern Japan display  $\delta^7\text{Li}$  as low as  $-17\text{‰}$ . These extremely light Li isotope ratios implicate the involvement of material from subduction-processed oceanic crust in the sub-continental mantle lithosphere represented by these nodules [71]. The samples also clearly document the possibility for large mantle  $\delta^7\text{Li}$  variations. In

a similar vein, Kobayashi et al. [72] report ion-probe data from Hawaiian olivine-hosted melt inclusions with  $\delta^7\text{Li}$  as low as  $-10\text{‰}$ . Nevertheless, this isotopically light component does not appear to represent a significant proportion of the source since it is not evident in the bulk lava compositions (Fig. 4A).

## 6. Implications

The observations above lead to some valuable inferences. For OIB, like MORB, a range of  $\delta^7\text{Li}$  points to variable amounts of recycled material in their sources. Very light Li isotope ratios from subduction-processed slab is dramatically evident in some mantle nodules and melt inclusions, but not in OIB lava compositions. Indeed, samples proposed to contain a large proportion of ancient basaltic slab are generally heavier than N-MORB. Likewise there is no evidence of lighter Li in samples frequently linked to a lower mantle reservoir. High  $^3\text{He}/^4\text{He}$  samples from Hawaii (type 3 Mauna Kea) have marginally higher  $\delta^7\text{Li}$  than N-MORB (Fig. 4A). Thus there is no indication of the drastic division in Li isotope signature between OIB and MORB that should result from subduction zone processing and preferential accumulation of subducted slabs in the lower mantle (e.g. [73]).

Clearly much more work is required to build on these initial observations. From the tantalising glimpse into the mantle provided by the current, we suggest that the trend to heavy  $\delta^7\text{Li}$  in OIB (and enriched MORB) sources has a common origin in the down-dragged mantle adjacent to the subducting slab (Fig. 3A). Fluids released from the down-going plate will be heavy, but variable in composition, depending on the prior history of dehydration. This process could account for the large variability in  $\delta^7\text{Li}$  not clearly related to other chemical tracers. Material from the slab has to pass into a hot portion of the mantle wedge before it triggers large-scale melting. The colder mantle layer overlying the slab will acquire a recycled signature, such as heavy  $\delta^7\text{Li}$ , from the passage of slab-derived fluids through it (Fig. 3A). The mantle layer may also similarly acquire

a sedimentary signature. This overlying mantle will be viscously coupled to the slab and so carried down beyond the subduction zone. As the slab descends and warms, the overlying enriched layer will cease to be viscously coupled. Depending on the thermal and dynamic history of the plate, the heavy  $\delta^7\text{Li}$  layer of mantle may be carried to variable depths to contribute to both MORB and OIB sources.

This scenario of recycling is still highly speculative. What is clear, however, from our current understanding of the behaviour of Li isotopes is that although there is ample evidence for the role of recycled material in some OIB and MORB sources, this does not appear to be in the form of subduction zone-processed mafic oceanic crust. Interestingly these sentiments are in keeping with other recent discussions on the geochemistry of OIB [5].

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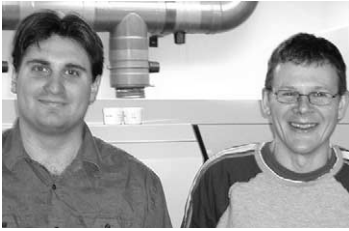
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